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APPLICATION OF VIBRATORS FOR MEASURING MORTAR CONSISTENCY AND FABRICATING MORTAR CUBES

By Raymond L. Blaine and John Tucker, Jr.

ABSTRACT

Two vibrators—one magnetic, with linear vertical motion; one mechanical with rotary horizontal motion—were employed to compact mortars of varying compositions, for various durations and at various frequencies and amplitudes. The effectiveness of the treatment was judged by (1) the reproducibility of the average strength of the six cubes in one batch, (2) the reproducibility of the strengths of individual specimens, and (3) the appearance of the compacted specimen. Standard Ottawa sand mortars possessed advantages over those with two or more types of aggregate. The mechanical rotary vibrator, designed for the investigation, was found to give better results than the magnetic vibrator. Either vibrator may be used to measure the consistencies of mortars of the dryness suitable for compaction by vibration.

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I. INTRODUCTION

The comparatively large variation in the values obtained in any of the physical tests of cement may be attributed at least in part to the human equation. Test results vary, not only between laboratories, but with different operators in the same laboratory and with the same operator from day to day and throughout the day. One of the variable

factors, but by no means the only one, which contributes to the differences in strength is the molding of the test specimens. In Europe, mechanically driven hammers or tampers have long been used to compact the mortar in an attempt to partially eliminate the personal equation. Experiments have been made with many different types of mechanical placing equipment [1, 2, 3].* Glanville [3] used a mechanically driven vibrator to compact the mortar cubes and obtained results more consistent than those usually obtained and also more indicative of the strengths that would be obtained with the same cements in concrete. There has also been a great deal of work done with mortars in an attempt to find some aggregates and gradings which are more suitable than those at present in use.

The investigation described in this paper had as its object the study of the strength and the strength reproducibility of mortars of various proportions and degrees of wetness when they were compacted by vibration. Hand fabricated mortar and concrete were made with the same cements for comparison.

II. APPARATUS AND MATERIALS

Two vibrators were used—an electromagnetic vibrator giving a simple harmonic motion along a vertical line, and a rotary vibrator giving a circular motion in a horizontal plane.

1. ELECTROMAGNETIC VIBRATOR

The electromagnetic vibrator was a commercial barrel packer, schematically shown in figure 1. The vibrating "head" of the machine is suspended by leaf springs, known as vibrator bars. An electromagnet to which alternating current is supplied attracts an armature fixed to these bars twice each cycle. This causes an attraction for both the positive and the negative halves of the wave; thus with 60-cycle current the frequency of vibration is 120 c/s. A rheostat in series with the electromagnet is used for varying the amplitude.

The vibrator had a sharp resonance characteristic. Changing the weight of the table by clamping one cube mold to it reduced the amplitude from its peak to so low a value that it could no longer be satisfactorily used for compacting specimens. On the other hand, if a body weighing several hundred pounds were placed on the vibrator and not fixed to the vibrating table, the amplitude would be adequate for compaction. In order to obtain an adequate amplitude with cube molds bolted to the head, it was therefore necessary to remove the head of the barrel packer and substitute a head of less weight to which molds could be fixed, so that the combined weight of head, molds, and mortar would be approximately that required to produce resonance. It was found necessary to work on one side of and just off the sharp resonance peak in order to obtain reproducible amplitudes. Figure 2 gives the resonance curve with the amplitude of vibration as a function of the table weight for a constant voltage producing a maximum amplitude of 0.021 in. This exceeds the maximum amplitude of 0.0156 in. recommended by the manufacturer of the machine in order that the safe armature clearance be not exceeded. It should be remembered in this connection that a small armature clearance is required for efficiency in an electromagnetic vibrator.

*Figures in brackets indicate the literature references at the end of this paper.

The molds were centered on the vibrating table. When mortar was placed in the molds, the amplitude was at first the same as that obtained with the empty molds; but as compaction was attained,

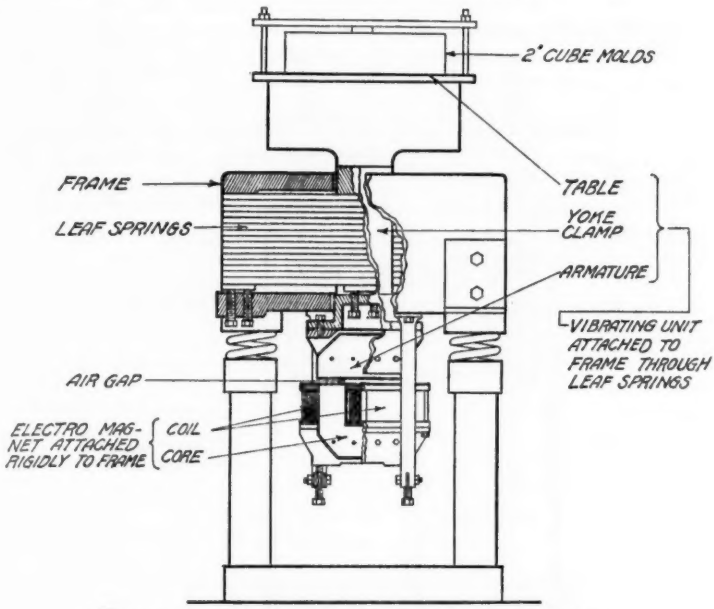

FIGURE 1.—*Electromagnetic vibrator, schematic view.*

the mortar became a part of the vibrating unit and, like a weight rigidly fixed to the head, reduced the amplitude of the vibrator. The

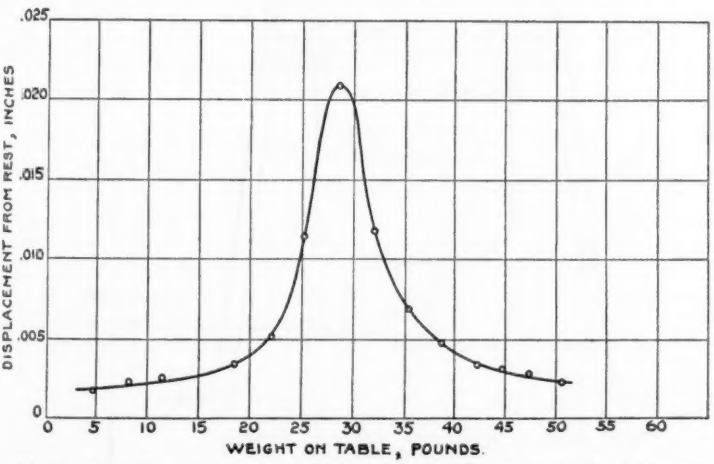

FIGURE 2.—*Resonance curve, electromagnetic vibrator: relation between amplitude and weight on table.*

vibrator, as contrasted with the motor-driven type, had the desirable characteristic of immediately attaining its full frequency and amplitude.

2. ROTARY VIBRATOR

The rotary vibrator, figure 3, designed for the present investigation, consisted of a circular vibrating table supported by six ¼-in.

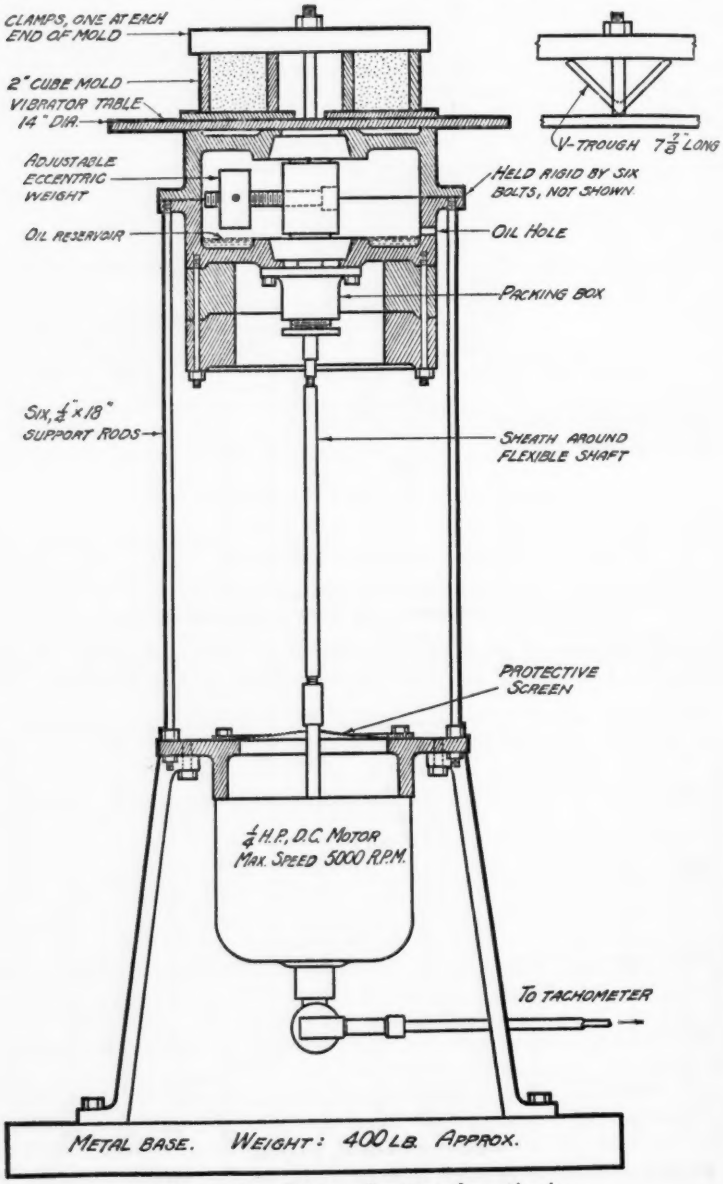
CLAMPS, ONE AT EACH END OF MOLD
2" CUBE MOLD
VIBRATOR TABLE 14" DIA.
ADJUSTABLE ECCENTRIC WEIGHT
OIL RESERVOIR
V-TROUGH 7⅞" LONG
HELD RIGID BY SIX BOLTS, NOT SHOWN.
OIL HOLE
PACKING BOX
SIX, ¼" × 18" SUPPORT RODS
SHEATH AROUND FLEXIBLE SHAFT
PROTECTIVE SCREEN
¼ H.P. D.C. MOTOR MAX. SPEED 5000 R.P.M.
TO TACHOMETER
METAL BASE. WEIGHT: 400 LB. APPROX.

FIGURE 3.—*Rotary vibrator, schematic view.*

diameter vertical steel rods 18 in. long. A variable-speed electric motor rotated by a flexible shaft an eccentric weight in the horizontal plane which passed through the center of gravity of the vibrating

table. The vibrator could be brought to its full speed of 83 c/s within 4 sec. The table with molds attached weighed about 120 lb.

The speed of rotation or frequency was controlled by resistance in the motor circuit, and the amplitude [1] was varied by using eccentric weights of different masses and also by adjusting their distance from the center of the rotating shaft. The motor speed was measured by means of a centrifugal type tachometer. The amplitude of the vibrator was approximately as computed theoretically from the relative mass of the eccentric weights, their eccentricity, and the total weight of table and molds, including eccentric weights. With the mortar compacted in the molds, the additional weight of the mortar theoretically reduced the amplitude 3 per cent; and this was found to be approximately correct, although it was difficult to measure the amplitude of the rotary vibrator because of the slight swinging of the table at its natural frequency.

The amplitude was constant within the range of speeds used. This system had two fundamental modes of low frequency—one a torsional mode with a period of about one-third second, about the axis of vibration, the other a flexural mode resulting in a circular motion of the same nature as the induced vibration but far larger in amplitude, having a period of about 1 second.

The amplitudes of both vibrators were measured with a micrometer microscope viewing an illuminated cross hair which was fixed on the vibrating unit. The measurements of amplitude are believed to be accurate to 0.0005 in. or better.

III. MATERIALS AND SPECIMENS

The portland cement used met the requirements of Federal Specification SS–C–191a. The cement was thoroughly mixed and then stored in airtight containers until batches were weighed out for mixing. As aggregates, standard Ottawa sand [2] (No. 20–30), fine (Ottawa) testing sand,[2] potters' flint, fine Potomac River sand, and No. 4 to ⅜ in. Potomac River gravel, largely quartz, were used. The flint was approximately 98 percent finer than 40 μ and had a specific surface of 3,400 cm^2/g. The Potomac River sand had a fineness modulus of 2.45.

Mortars were mixed as prescribed in Federal Specification SS–C–158, paragraph F–4m(2), with batches of such size that there was sufficient mortar to fill two three-gang molds. Two methods of placing the mortar in the molds were employed. In one method the molds were vibrated as they were being filled in three approximately equal layers, requiring about 1 min. After the molds were filled, vibration was continued for another minute. In the second method, the molds were filled to heaping, the vibrator started, and the molds were vibrated for 60 sec from the time the testing speed was attained. After the vibration period, the mortar above the tops of molds was cut off with a sawing motion of the straight edge of a trowel held at an angle of about 45° from the horizontal. No other troweling or smoothing was employed. Specimens were stored in the damp closet for 20 hr at 70°±2°F and relative humidity of 95 percent or higher. They were then stored in water at 70°±2°F until tested in compression.

[1] Amplitude is the maximum displacement from position of rest. The total excursion of the head is twice the amplitude.

[2] Federal Specification SS–C–158.

The comparison group of hand-compacted cubes was fabricated according to the method prescribed in Federal Specification SS–C–158.

The cubes upon which the air voids were determined were removed from the molds at the end of 20 hr and weighed. The water, cement, and aggregate were assumed to be present in the proportions as mixed, and their total bulk was computed. The difference between this value and the bulk of the 2-in. cube (8 in.^{3}) was tabulated as the air voids. Thus, voids caused by any irregularity in the top of the cube (fig. 4) were included in the computed air voids.

The 6- by 12-in. concrete cylinders were proportioned 1:2.2:3.8, by weight, of cement, Potomac River sand, and No. 4 to 1½ in. Potomac River gravel. Three cylinders were made with C/W ratio of 1.7 and three with a C/W ratio of 2.0. The cylinders were rodded by the usual ASTM method. They were kept in the damp storage until test.

Compression tests of all specimens were made at the age of 7 days. In the testing of all cubes the load was applied at the rate of 6,000 pounds per square inch per minute; in the testing of concrete cylinders the load was applied at the rate of 500 pounds per square inch per minute.

IV. TESTS

1. MOVEMENT OF MORTAR IN MOLD (ROTARY VIBRATOR)

Studies were made of the motion of the mortar during vibration by using black and white mortars placed in definite patterns in the mold and also by measuring the rotation of the mortar within the molds during vibration.

(a) STUDY OF MOVEMENT BY STRATIFIED MORTARS

During vibration on the rotary vibrator, the mortar continuously rotated about the vertical axis of the mold. A study was therefore made to determine whether this movement had any undesirable features. The vibrator was operated at a speed of 40 c/s with an amplitude of 0.03 in. A white portland cement standard Ottawa sand mortar (proportions 1:3.5 by weight) with varying percentages of mixing water, and the same mortar colored by carbon black were placed in the molds in strata and were vibrated a short time to determine if segregation occurred other than that which could be observed on the tops of the cubes. At the end of 24 hr the cubes were removed from the molds and split open. Figure 5 shows a group of four such cubes of mortars with 10 percent of mixing water. The two broken halves of each of the four cubes are shown. In the upper left cube, white mortar was placed in the lower half, black in the upper half. In the upper right cube, a vertical cylinder of black mortar was placed in the surrounding white mortar. The mortar in the lower two cubes was placed in two parts, white on the front left side, black in the rear right side. The motion of the mortar was upward in the center of the mold and downward at the sides, as can be seen in the two upper cubes. The upper portion of the mortar had rotated through a greater angle than had the mortar at the bottom of the mold, as shown by the two cubes at the bottom of the figure.

The motion is largely laminar, the turbulence or intermixing of the mortars of different color being small in dimension. Neither in the mortars shown in figure 5 nor in the other drier mortars was there any evidence of segregation of cement or of water. If the mortar

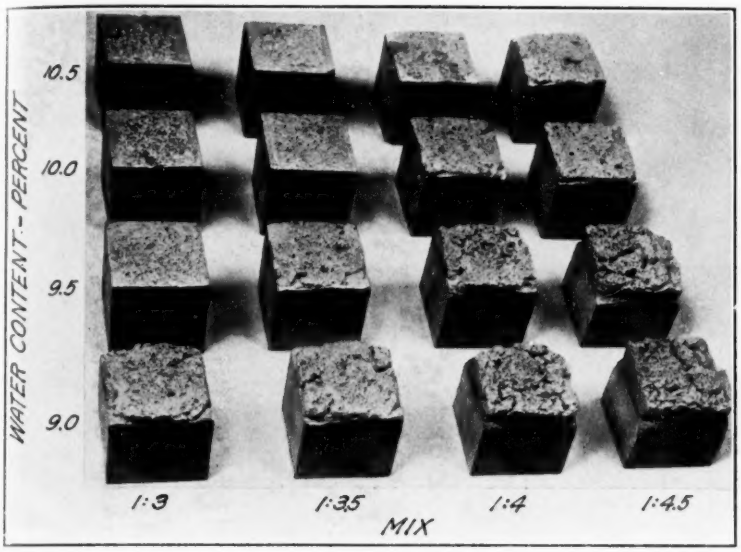

FIGURE 4.—*Extent of compaction as shown by condition of mortar in cubes.*

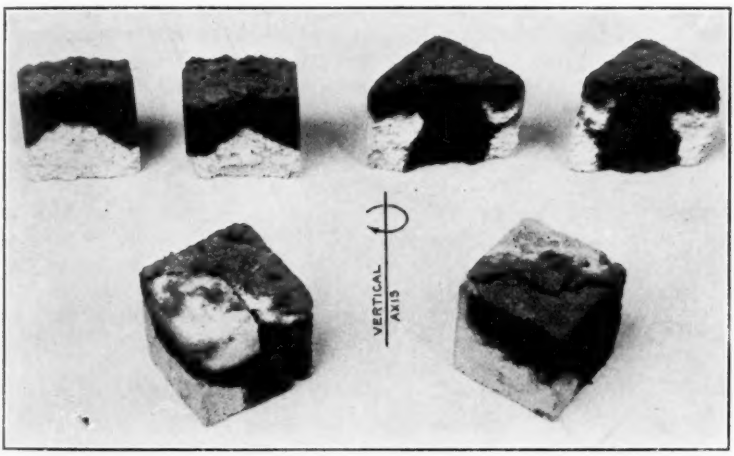

FIGURE 5.—*Cubes of colored mortars showing the movement of mortar caused by vibration.*

was too dry, containing say in the proximity of 8 percent of mixing water, the molds were not filled, the mortar first forming into approximately a 2-in. diameter cylinder, with axis vertical, after which the corners of the mold commenced filling. In the mixes with more water (9 percent or greater) the corners of the molds were always filled as the mortar rotated. The movements of the mortar were greater with the drier mixes.

(b) STUDY OF ROTATION OF MORTARS

The movement of the mortars in the molds on the rotary vibrator was also studied by measurement of the rotation by means of metal can covers about 2 in. in diameter through which four wire brads were driven with the heads firmly soldered in place. The brads were placed equidistant from the center of the cover and equally spaced on the circumference. Various length brads from ⅜ in. to 1½ in. were used. The 1-in. brads appeared to be the most satisfactory. The covers with short brads rotated more than those with long brads, indicating as with the varicolored mortars that the mortar on top rotated more than that at the bottom of the mold.

In measuring the angle of rotation, the molds were first filled with mortar and the covers were then placed in contact with the upper surface of the cube with the brads in the mortar. The cube molds were then vibrated for 1 min, and the angle of rotation of the covers was measured. The rate of rotation of the cover was initially rapid. It decreased gradually and approached a constant value, until after a certain time the rate of rotation was quite constant. The initial rate varied as did the time required to assume a constant rate, depending upon the richness and wetness of the mortar. Since the rate of rotation of all mortars was approximately the same after the rate became constant, it could not be used to differentiate between mortars of varying consistency.

A series of tests was made using one batch of each of the standard Ottawa sand mortars with water contents of 9, 9½, 10, and 10½ percent. The mortars were compacted for 1 min on the rotary vibrator at 40 c/s and 0.030-in. amplitude. The rotation of the can covers during the first minute is plotted on a logarithmic scale against the C/W ratio in figure 6. This leads to a family of approximately straight lines independent of the cement-sand ratios. Dotted lines connect mortars with the same percentage of water.

The values shown in figure 6 are averages of six measurements on one batch, it being desirable to have at least that number of measurements to secure a sufficiently reliable value. Although conceivably such an average value would give some indication of the consistency of the mortar, the method was considered too tedious and subject to too great an experimental error for use as a routine test method.

2. FLOW OF MORTARS ON FLOW TABLE AND ON VIBRATORS

(a) FLOW ON A FLAT PLATE

The diameters of mortar specimens were measured at intervals of five drops of the flow table.[3] The increase in diameter from the original diameter at each number of drops has been termed the "flow" for that number of drops. The data are given in figure 7. As may be

[3] Federal Specification SS-C-158.

seen from this figure, the different curves for the dry standard Ottawa sand mortar have greatly varied shapes and do not arrange themselves in a simple sequence. This is in decided contrast to the similar shapes and regular sequences of the corresponding curves for the fine testing sand mortars of wetter consistency. It can be seen that for each cement-sand ratio these curves are arranged in order of increasing water content and also that for each water content the curves are arranged in order of increasing richness of cement.

The ogee form or change in curvature of the curves at the right of figure 7 is ascribed in general to the breaking or splitting of the mortar

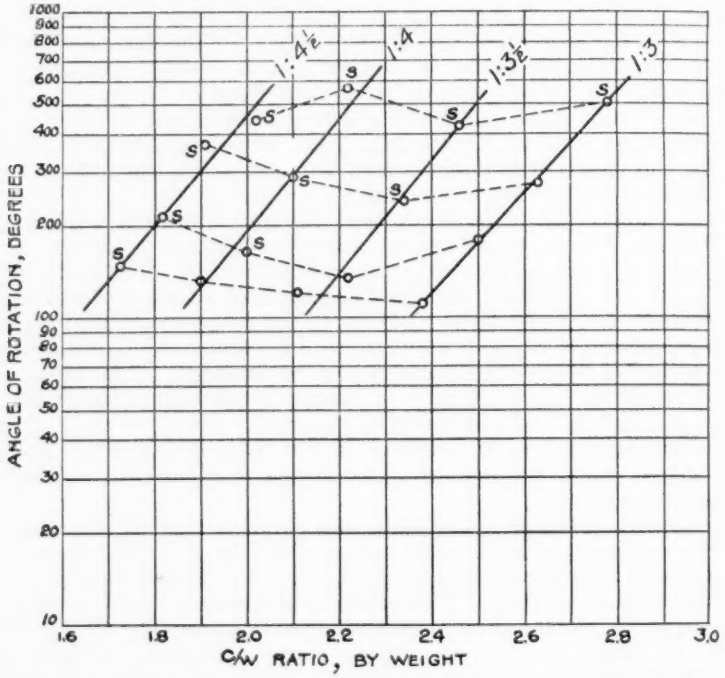

FIGURE 6.—*Relation between angle of rotation during the first minute vibration and C/W ratios.*

The points marked *S* indicate mixes whose cubes in figure 4 showed incomplete compaction.

into two or more parts by reason of its dryness and the rapid spread of the parts which are no longer mutually restrained when the splitting occurs.

The diameters of standard Ottawa sand mortar specimens were measured at intervals of 5 sec during vibration on a flat plate on both the magnetic and rotary vibrators. The hollow truncated cone used with the 10-in. flow table was placed on the flat plate fastened to the motionless vibrator and was filled with mortar in the standard manner to form the mortar specimens. The increase in diameter of the mortar specimens at any time was termed the "flow" for that duration of vibration.

The flow of mortars on the flat plate fastened to the rotary vibrator has several undesirable characteristics. The mortar upon start of

vibration does not immediately flow but slips about on the plate for an indefinite short period, after which flow starts. When the mortar begins to flow it loses its circular perimeter, the outer edge assuming very irregular shapes. The curves of the flow of this mortar with time are intermediate in their regularity between the two groups

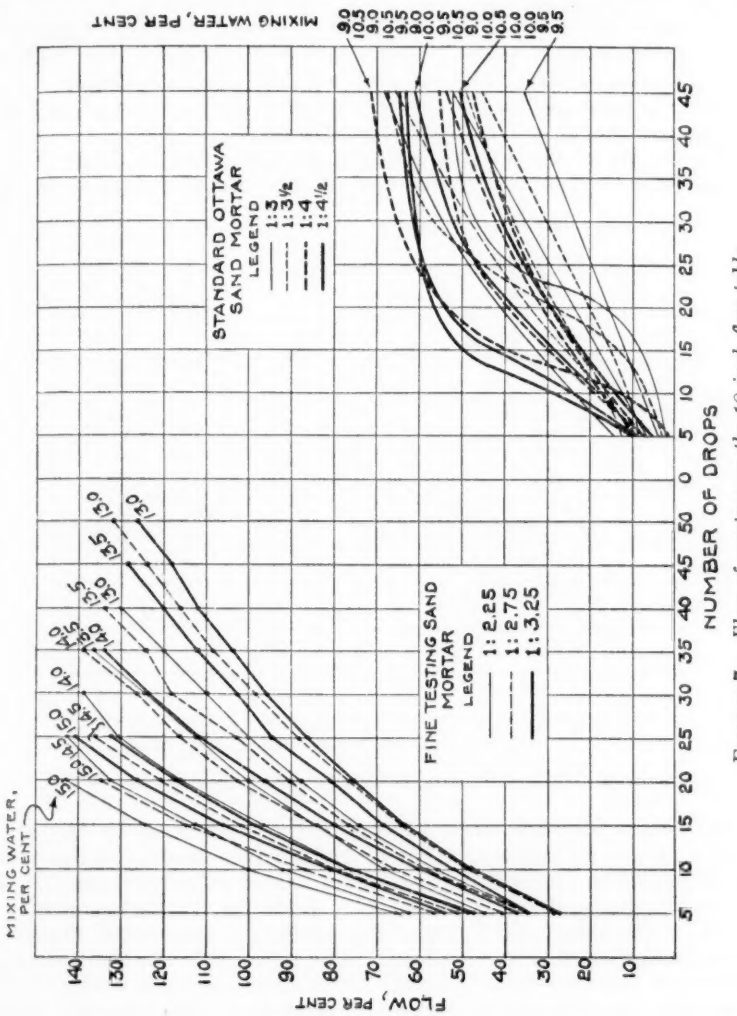

FIGURE 7.—*Flow of mortars on the 10-inch flow table.*

shown in figure 7. For these reasons this test method is not recommended.

The flow of standard Ottawa sand mortars on the magnetic vibrator, flat plate, is shown in figure 8. These curves are in nearly as definite a sequence as those for the fine testing sand mortars on the flow table, shown at the left in figure 7.

(b) FLOW IN A V-TROUGH

The flows of mortar were also determined in a V-trough made of structural-steel angle attached to the vibrators, as illustrated in figure 3. The mortar was placed in the trough in the space between two vertical plates 2 in. apart and perpendicular to the axis of the trough. The mortar was filled flush with the top of the trough, with just enough working to compact it as in the standard method of filling the flow-table mold. The vertical plates were then removed and vibration started. The length of the mortar specimen in the trough was measured every 10 sec for 1 min. The increase in length was termed the "flow" for each time interval.

The results of the V-trough flow tests are given in figure 9. Although there was some irregularity in the flow, the results obtained

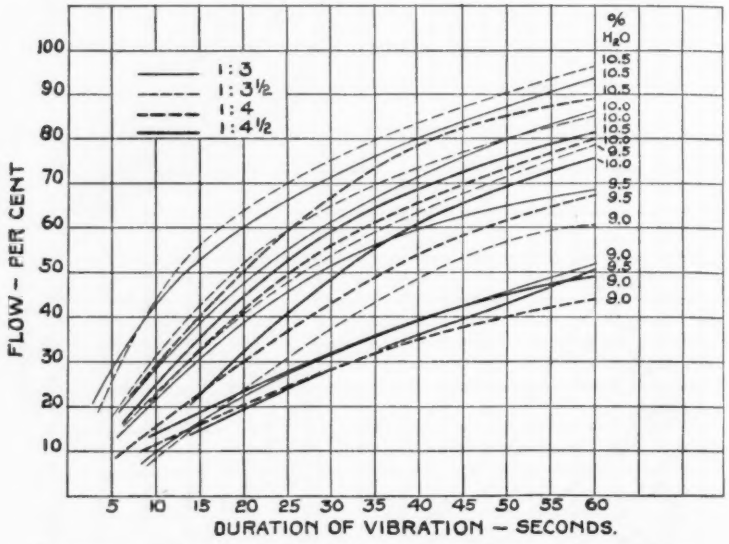

FIGURE 8.—*Flow of mortars on flat plate on electromagnetic vibrator.*

on the rotary vibrator were the best of those obtained by any of the three methods of measuring flow of dry mortars, insofar as the curves are arranged most nearly in ascending values of percentage of water and in increasing richness of cement. Even for the short duration of 20 sec of vibration, the flows of the mortars are arranged exactly in ascending order of water content. The measurements thus made on the rotary vibrator with V-trough have characteristics similar to the flow-table measurements made on wetter plastic mortar mixes, intended for hand compaction, such as those described in Federal Specification SS-C-158.

From the few studies made of like batches, it appeared that the reproducibility of mortar flows in the V-trough, rotary vibrator, was approximately the same as that of 1:2.75 fine testing sand mortars with a flow of 100 to 115 (25 drops), as made on the standard 10-in. flow table. (See fig. 7.)

The flow curves for the mortars in the V-trough on the magnetic vibrator gave fairly good results but were not arranged in as definite a

sequence as for the flat plate on the same vibrator, or in the V-trough on the rotary vibrator.

The tests show that the V-trough on the rotary vibrator, or the flat plate on the magnetic vibrator may be used to measure the consistency in mortars of the dryness required for compaction by vibration. Measurements on vibrators may thus be used for dry mortars in place of the standard 10-in. flow table, which is suitable only for the wetter or plastic mortars.

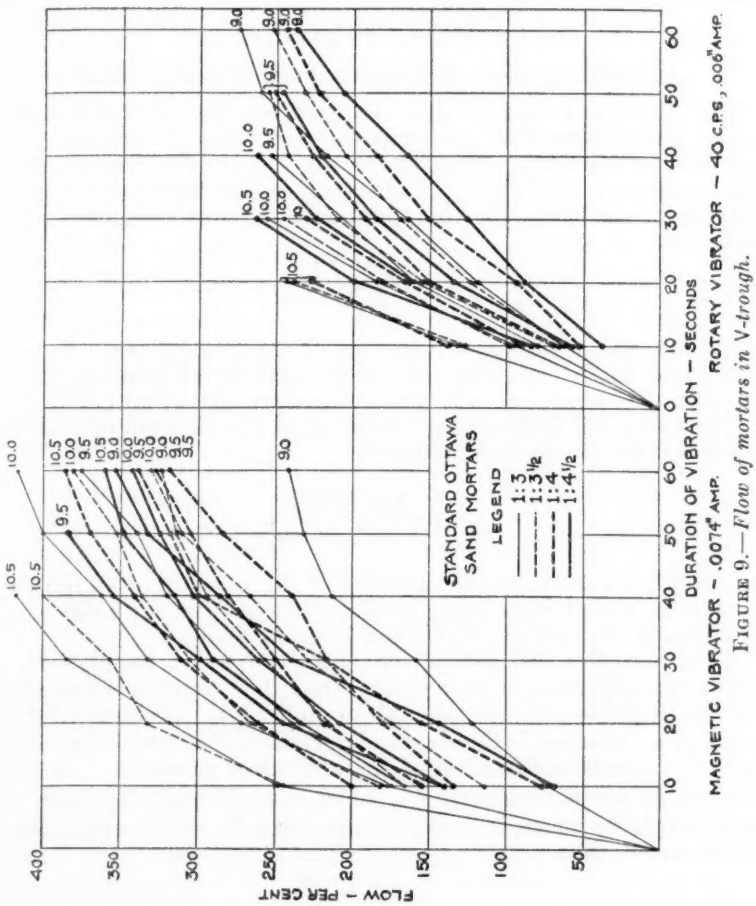

FIGURE 9.—*Flow of mortars in V-trough.*

3. NONHOMOGENEOUS COMPACTION OF MORTARS

The strengths and solidities of the cubes are not wholly adequate criteria for determining the degree of the compaction. In some mixes compacted by vibration the compaction was not homogeneous throughout the cube, although the body of the cube was compact and strong. An upper layer of incompletely compacted mortar was present in the upper portion of the cube. This is illustrated in figure 4 for cubes of cement and standard sand in different proportions and with differ-

ent amounts of water. The specimens were vibrated for 1 min. on the rotary vibrator, 40 c/s, 0.031-in. amplitude.

The specimens in the diagonal row from lower left to upper right were almost completely compacted throughout to an equal degree, as visually estimated. The compaction of the cubes became increasingly poor and nonhomogeneous in passing below the foregoing diagonal. This was accompanied by an increase in the amount of incompletely compacted mortar on top of the cubes. The compaction of all cubes *above* the diagonal was practically perfect.

4. STRENGTH OF SPECIMENS

(a) REPRODUCIBILITY OF STRENGTH—THEORY OF MEASUREMENT

The strength reproducibility, both of batches and of individual cubes, was expressed by means of the coefficient of variation.[4] The smaller the coefficient of variation the greater the reproducibility. The estimated coefficient of variation of the average strength of batches of six cubes (batch reproducibility) was computed by the formula

$$C_b=\frac{100}{s}\sqrt{\frac{\Sigma v^2}{n-1}}, \tag{1}$$

where v is the deviation or variation of the average strength of the individual batch from the average strength of all batches, n is the number of batches, and s is the average strength of all batches.

The estimated coefficient of variation of the strength of individual cubes was computed by the formula

$$C_i=\frac{100}{s}\sqrt{\frac{\Sigma v_i^2}{N-n}}, \tag{2}$$

where v_i is the deviation or variation of the strength of an individual cube from the average strength of its batch, N is the total number of cubes in the batches, and s and n are as above.

In a normally distributed universe [4] (parent population) and where the dispersion in the average strength of batches is caused only by the dispersion of the strength of individual specimens, we have $\sigma_b=\sigma_i/\sqrt{n_0}$, where σ_b is the standard deviation of a batch of size n_0 and σ_i is the standard deviation of the individual specimen. It is convenient to use a parameter $\overline{C}_b$, which we will call the ideal value of $C_b=C_i/\sqrt{n_0}$, which is based on the normally distributed universe. When $n_0=6$, then

$$\overline{C}_b=0.408C_i \tag{3}$$

(b) HAND-COMPACTED SPECIMENS

The compressive strength of a 1:2.2:3.8 (by weight) concrete was determined from 6- by 12-in. test cylinders. Two water contents were used; the C/W ratios were 1.71 and 2.00, the concretes had flows (fifteen ⅛-in. drops on the 30-in. flow table) of 25 and 8, slumps of 1¾ and ¼ in., and 7-day strengths of 2,825 and 3,250 lb/in.^{2}, respectively.

[4] The coefficient of variation is the standard deviation expressed in percentage of the mean value.

A number of cubes were made in accordance with the requirements of Federal Specification SS–C–158, proportions 1:2.75, cement to fine testing sand, by weight, with just enough mixing water to give a flow of 100. The cubes were made by four operators each of whom made one batch of six cubes a day. The test results are given in table 1. The average strength of the cubes was 2,900 lb/in.^{2}, equal to the strength of the 1:2.2:3.8 concrete with a water content corresponding to approximately $C/W=1.7$. The average coefficient of variation of the strength of batches (C_b) is 3.8. This is the day-by-day variation in the strength obtained by the four operators.

TABLE 1.—*Data on hand-compacted plastic mortar cubes (fabricated by method of Federal Specification SS–C–158)*

Operator [1]	Mean compressive strength	Coefficient of variation		Voids
		C_b	C_i	
	lb/in.^{2}			*Percent*
A	2,850	0.9	3.3	
B	2,900	4.4	3.7	
C	2,900	4.4	4.1	
D	2,940	4.5	2.8	
Weighted mean	2,900	3.8	3.5	7.3

[1] Operator *A* made 3 groups of 6 cubes; operators *B*, *C*, and *D* made 6 groups of 6 cubes. Each operator made but 1 group on any one day. Specimens tested at 7 days.

It is of interest to note that the variation between batches is not attributable to the scatter in the strength of individual cubes. If the scatter in the batch strength were due to the scatter in the strength of the individual cubes, the coefficient of variation of the batch strength ($\overline{C}_b$) would be, from eq 3, 0.408 C_i or $0.408\times3.5=1.4$. The average C_b from table 1 is 3.8, almost three times this value, indicating a day-by-day or batch-to-batch variation much greater than that caused by the scatter in the strengths of individual cubes in a batch.

It may be noted that the average strengths obtained by the several operators are in remarkable agreement. Statistical analysis shows that the variation in the strengths obtained by the different operators is no greater than the variation which would be expected if one operator had made all the specimens.

(c) MORTAR SPECIMENS COMPACTED BY VIBRATION

(1) *Study of different aggregates and proportions.*—Preliminary studies of compaction by vibration were made on mortars of various proportions, with various combinations of the aggregates, and vibrated for varying durations and with various amplitudes and frequencies of vibration. Tables 2, 3, and 4 summarize the results of these tests. The mixes of table 2 were compacted by the rotary vibrator; the three "pebble" mixes of table 3 were compacted under two accelerations each for the rotary and for the magnetic vibrator. The mixes of table 4 were compacted on the rotary vibrator with an amplitude of 0.007 in. and frequencies of 33 to 83 c/s.

From table 2 it is immediately apparent that, with the exception of one of the three mixes containing potter's flint, the strengths were considerably above the strength of 2,900 lb/in.^{2} of the hand-fabricated plastic mortar cubes, and that with the mixes containing gravel much higher strengths could be obtained.

TABLE 2.—*Data on mortars with several aggregates in varying proportions*

[Compacted on rotary vibrator, 83 c/s, 0.007-in. amplitude. Molds first filled, then vibrated]

Proportions, parts by weight						Cement/water ratio, by weight	Compressive strength [a]	Coefficient of variation, C_i
Cement	Potter's flint	Fine testing sand	Standard Ottawa sand	Gravel No. 4 to ⅜ in.	Water, percentage by weight, dry mix			
							lb/in.²	
0.6	0.4	0	3	0	10.0	1.50	2,000	2.8
.7	.3	0	3	0	10.0	1.75	3,520	2.3
.8	.2	0	3	0	10.0	2.00	5,150	2.6
1.0	0	0	3	0	9.5	2.63	4,800	1.8
1	0	0	3.25	0	9.5	2.48	4,260	2.1
1	0	0	3.5	0	9.5	2.33	3,480	0.9
1	0	0.5	3	0	10.0	2.35	3,700	4.0
1	0	1.0	2.5	0	10.0	2.22	3,960	1.9
1	0	1.0	2.5	0	10.0	2.22	3,730	2.4
1	0	1.0	2.5	0	10.0	2.22	3,600	2.1
1	0	1.5	2.0	0	10.0	2.22	3,970	2.2
1	0	2.0	1.5	0	10.0	2.22	4,250	1.9
1	0	2.0	1.5	0	10.0	2.22	4,030	1.4
1	0	2.0	1.5	0	10.0	2.22	3,640	1.9
1	0	2.5	1.0	0	10.0	2.22	4,160	1.7
1	0	3.0	0.5	0	10.0	2.22	4,390	1.6
1	0	0	2.0	2.0	8.0	2.50	6,080	3.4
1	0	0	2.0	2.5	7.55	2.41	6,070	2.7
1	0	0	2.0	3.0	7.15	2.33	6,120	3.2
1	0	0	2.5	2.5	7.6	2.19	4,580	2.8
1	0	0	2.75	2.5	7.6	2.19	4,450	2.1
1	0	0	3.0	2.5	7.6	2.19	4,330	2.3
1	0	0	3.25	2.5	6.95	2.14	4,100	2.2
1	0	0	3.25	2.5	7.4	2.00	3,360	2.6
1	0	0	3.5	2.5	6.7	2.14	3,920	2.6
1	0	0	3.0	2.5	7.15	2.00	4,400	3.1
1	0	0	3.0	3.0	7.15	2.00	3,600	3.4
1	0	0	3.5	3.0	6.67	2.00	3,570	3.6

[a] Specimens tested at 7 days.
Each line represents tests of 18 cubes.

TABLE 3.—*Data on three "pebble" mortars [a] compacted by vibration*

Each strength given is the average of 6 batches of 6 cubes, tested at the age of 7 days. Molds filled, then vibrated]

Vibrator	Acceleration, *g*	Duration	Bates mix			Bates mix modified			Pearson mix modified		
			Compressive strength	Coefficient of variation		Compressive strength	Coefficient of variation		Compressive strength	Coefficient of variation	
				C_b	C_i		C_b	C_i		C_b	C_i
		Seconds	*lb/in.²*			*lb/in.²*			*lb/in.²*		
Magnetic	[b] 7.3	30	4,330	2.9	2.6	4,920	3.6	2.6	3,720	4.0	3.9
Do	[b] 7.3	60	4,420	2.0	2.5	4,780	3.3	2.4	3,700	1.3	2.7
Do	[b] 7.3	90	4,370	1.9	2.5	4,800	4.0	3.0	3,750	2.5	3.0
Do	[c] 16.5	30	4,410	2.9	2.7	5,000	3.1	3.7	4,110	4.6	3.6
Do	[c] 16.5	60	4,550	4.0	3.2	4,980	3.5	3.7	4,140	4.6	3.3
Do	[c] 16.5	90	4,550	3.0	3.1	5,080	3.2	3.1	4,260	5.4	3.3
Mean			4,420	2.8	2.8	4,920	3.4	3.1	3,950	3.7	3.2
Rotary	[d] 4.2	30	4,360	1.0	2.0	4,760	2.1	1.8	3,800	4.2	1.8
Do	[d] 4.2	60	4,420	1.3	2.4	4,710	1.3	2.4	3,840	4.5	2.4
Do	[d] 4.2	90	4,480	2.4	2.7	4,850	2.1	2.5	3,820	7.1	2.1
Do	[e] 10.5	30	4,490	3.5	2.4	4,980	2.5	1.8	4,150	4.1	2.6
Do	[e] 10.5	60	4,610	2.9	2.1	4,830	2.1	2.3	4,200	2.6	2.2
Do	[e] 10.5	90	4,640	2.8	2.3	4,900	2.2	2.5	4,300	2.9	2.3
Mean			4,500	2.3	2.3	4,840	2.1	2.2	4,020	4.2	2.2

See footnotes at end of table.

TABLE 3.—*Data on three "pebble" mortars compacted by vibration*—Continued

MIX PROPORTIONS BY WEIGHT, IN GRAMS

Component	Bates	Bates modified	Pearson modified
No. 4 to ¾ in. gravel	1,080	1,080	1,000
Standard 20-30 Ottawa sand	632	540	416
Fine Potomac River sand			252
Potters' flint	88	108	
Cement	360	432	300
Water	191	216	160

[a] Based on mixes proposed for study by Committee C-1, ASTM; Proc. Am. Soc. Testing Materials 38, p. 1, 268 (1938).
[b] Amplitude, 0.0035 in. to 0.0065 in.; frequency, 120 c/s; acceleration, 5.1 to 9.5 *g*; average, 7.3 *g*. Initial amplitude 0.0065 in., reducing to 0.0035 when mortars were compacted.
[c] Amplitude, 0.0075 in. to 0.0150 in.; frequency, 120 c/s; acceleration, 11.0 to 22.0 *g*; average, 16.5 *g*.
[d] Amplitude, 0.006 in.; frequency, 83 c/s; acceleration, 4.2 *g*.
[e] Amplitude, 0.015 in.; frequency, 83 c/s; acceleration, 10.5 *g*.

TABLE 4.—*Data on effect of different speeds and durations of vibration*

Compacted on rotary vibrator; amplitude, 0.007 in. Molds first filled, then vibrated. Mortar: 1:3.5 standard Ottawa sand; 10 percent mixing water.]

Speed	Duration	Acceleration, *g*	Number of specimens	Voids	Compressive strength [a]	Coefficient of variation, C_i
c/s	*Seconds*			*Percent*	*lb/in.²*	
33	20	0.8	6	16.7	2,380	3.4
33	40	.8	6	16.5	2,400	3.5
33	60	.8	18	16.5	2,390	4.2
33	90	.8	6	15.6	2,570	2.2
50	20	1.8	6	14.4	2,830	1.6
50	40	1.8	6	13.9	3,030	1.1
50	60	1.8	18	13.5	3,220	2.5
50	90	1.8	6	13.1	3,350	0.9
67	20	3.2	6	13.1	3,350	2.6
67	40	3.2	6	13.1	3,620	2.4
67	60	3.2	18	12.7	3,600	2.1
67	90	3.2	6	12.3	3,710	1.0
83	20	5.0	18	13.1	3,640	2.2
83	40	5.0	18	13.1	3,750	1.7
83	60	5.0	[b] 36	12.3	3,820	1.5
83	90	5.0	18	12.3	3,930	1.7

[a] Specimens tested at 7 days.
[b] Six cubes each by 6 operators.

The average value of C_i for the several types of mixes is as follows: 3 series of standard sand, 1.6; 10 series of standard and fine sand, 2.1; 3 series of flint and standard sand, 2.6; 12 series of gravel, 2.8. With two exceptions the mixes compacted by vibration had better reproducibility than the mean reproducibility of the hand-compacted specimens.

The three mixes of table 3 compacted on the rotary vibrator had in general slightly less strength dispersion than the gravel mixes of table 1, and a greater strength dispersion than the mixes with both fine testing sand and standard Ottawa sand or with standard Ottawa sand of the same table. The mixes of table 2 were so wet that they compacted rapidly, little being gained by vibrating more than 30 sec., since cement and water splashed from the mold during vibration. The mixes were obviously too wet and should not be given much consideration.

From table 3 it is seen that the Pearson mix is sensitive to differences in the intensities of vibration from approximately 7.0 to 15.6

g in the magnetic vibrator and 4.2 to 10.5 *g* in the rotary vibrator, the "modified" Bates mix shows a slight difference, and the Bates mix shows the unappreciable difference of approximately 150 lb/in.,^{2} due to the difference in vibration intensities. The intensities of vibration on the magnetic vibrator were adjusted to give final (and lowest) values of acceleration of 5.1 and 11.0 *g*, approximating the accelerations of 4.2 and 10.5 *g* of the rotary vibrator.

When compacted on the rotary vibrator, the batch reproducibilities of the two Bates mixes are about equal, and much better than the Pearson mix. The batch reproducibility of the Bates mixes was better on the rotary than on the magnetic vibrator.

From a study of the results of the tests summarized in tables 2 and 3, it may be concluded that the mixes with only cement and standard Ottawa sand had slightly better batch reproducibility than any of the other mixes.

(2) *Effect of duration, amplitude, and frequency of vibration.*—A series of tests was made of a 1:3.5 standard Ottawa sand mortar, 10 percent water, to study the effect of duration and speed on compaction and strength. The mortars were compacted on the rotary vibrator (amplitude of vibration 0.007 in. at speeds of 33 to 87 c/s and with durations of from 20 to 90 sec). The results of the tests are summarized in table 4.

Little strength was gained by vibrating for more than 40 sec. In general, the strength dispersion at 33 c/s was about that for hand-compacted specimens and, for speeds of 50 c/s or greater, was approximately half this value. The greatest strength was attained in all cases in 90 sec of vibration. The strength increased with the frequency of vibration by an amount which decreased in approaching the top speed of 83 c/s.

Some insight into the degree of compaction may be gained from the percentage of air voids in the specimens. The mortar, if completely compacted, would have, theoretically, no voids. According to table 4 the percentage of air voids ranged from 12.3 to 16.7. None of the mortars were therefore completely compacted; but those compacted at the two higher speeds had less voids than those compacted, for the same duration, at 50 c/s, and those compacted at 50 c/s had less voids than those compacted for equal durations at 33 c/s. Moreover, the longer the vibration, in general, the less the voids, for any one frequency of vibration. There is a definite correlation between the strength of the specimen and the quantity of air voids.

Additional data on the effect of amplitude, frequency, and duration of vibration on compaction were furnished by the three "pebble" mortars (see table 3). In these mortars the change in strength by vibrating longer than 30 sec was slight.

(3) *Study of standard Ottawa sand mortars.*—The preliminary studies having indicated the general type of mortars that would be most satisfactory for compaction, and the necessary vibration characteristics, another series (table 5) was prepared primarily to measure the reproducibility or uniformity of strength of individual specimens and of batches. The proportions used in this latter study were 1:3, 1:3.5, 1:4, and 1:4.5, parts of cement to parts of standard Ottawa 20–30 sand, by weight. With each proportion four different water contents were used—namely 9.0, 9.5, 10.0, and 10.5 percent of water by weight of the dry mix. Mortars were compacted at one amplitude

on the magnetic vibrator and at two amplitudes at two speeds on the rotary vibrator.

Two methods of filling the molds were used: The first consisted in filling the molds to heaping and then vibrating them, and the second consisted in filling the molds in three layers while they were vibrating.

The values marked with asterisks indicated cubes which were not homogeneously compacted and had defective top portions. These cubes will not be considered in the discussion. Figure 4 shows one cube from each of the 16 groups which were compacted on the rotary vibrator at 40 c/s by vibrating the molds after filling; a number of cubes in this figure have defective tops.

TABLE 5.—*Characteristics of standard Ottawa sand (20–30) mortars compacted by two vibrators by two methods of filling molds*

[Duration of vibration, 1 minute. Specimens tested at 7 days. Each strength given is the average of 6 batches of 6 cubes]

Proportions by weight	Water content	Molds vibrated as filled					Molds filled, then vibrated				
		Air voids	Compressive strength	Strength dispersion			Air voids	Compressive strength	Strength dispersion		
				C_b	$\overline{C}_b$	C_i			C_b	$\overline{C}_b$	C_i
Rotary vibrator—frequency, 40 c/s; amplitude, 0.031 in.; acceleration, 5 *g*											
	Percent	*Percent*	*lb/in.²*				*Percent*	*lb/in.²*			
1:3	9.0	7.8	* 6,370	2.5	3.0	7.3	10.7	* 5,560	3.5	2.5	6.1
1:3	9.5	7.0	6,130	2.5	0.8	2.0	8.5	5,740	3.2	1.1	2.7
1:3	10.0	8.3	5,290	2.9	.9	2.3	9.2	5,160	2.9	0.6	1.5
1:3	10.5	8.6	4,740	2.3	.9	2.1	9.9	4,740	3.4	.9	2.2
1:3.5	9.0	8.8	* 5,020	3.5	1.5	3.6	11.7	* 4,240	3.2	1.6	3.8
1:3.5	9.5	7.4	* 4,930	1.7	0.7	1.8	9.9	* 4,390	3.1	0.9	2.3
1:3.5	10.0	8.5	4,200	2.5	1.0	2.5	10.6	3,920	1.2	.8	2.0
1:3.5	10.5	8.8	3,680	1.9	0.9	2.3	10.1	3,540	2.1	.7	1.8
1:4	9.0	13.5	* 2,980	2.9	3.3	8.1	14.9	* 2,820	4.5	1.8	4.5
1:4	9.5	10.4	* 3,440	1.7	2.2	5.5	12.5	* 3,030	3.1	1.9	4.6
1:4	10.0	8.1	* 3,480	2.9	1.3	3.1	11.5	* 2,990	1.4	1.3	3.2
1:4	10.5	8.5	3,010	1.2	0.8	2.0	10.6	2,750	1.6	0.7	1.7
1:4.5	9.0	15.7	* 1,980	6.6	4.1	10.0	17.6	* 1,820	5.1	3.7	9.0
1:4.5	9.5	12.7	* 2,350	7.8	3.1	7.6	14.3	* 2,090	5.9	2.5	6.1
1:4.5	10.0	10.1	* 2,510	3.2	2.4	5.8	12.6	* 2,180	2.3	1.7	4.2
1:4.5	10.5	9.0	* 2,320	1.9	1.6	4.0	11.7	* 2,010	2.6	1.3	3.2
Rotary vibrator—frequency, 83 c/s; amplitude, 0.007 in.; acceleration, 5 *g*											
1:3	9.0	9.1	6,470	2.0	0.8	2.0	9.9	6,100	3.1	0.9	2.2
1:3	9.5	10.1	5,660	2.6	1.2	3.0	10.6	5,530	1.3	.9	2.1
1:3	10.0	11.3	5,030	2.8	1.2	3.0	11.3	4,970	4.0	.6	1.6
1:3	10.5	11.6	4,570	2.8	1.2	3.0	11.6	4,590	2.9	1.0	2.4
1:3.5	9.0	11.3	4,840	2.0	0.9	2.3	11.7	4,700	1.3	0.7	1.8
1:3.5	9.5	11.6	4,300	1.1	.9	2.3	12.4	4,260	1.8	.6	1.4
1:3.5	10.0	12.7	3,900	2.1	1.1	2.8	12.7	3,820	0.9	.8	2.0
1:3.5	10.5	12.2	3,490	0.7	1.0	2.5	12.6	3,460	.8	.9	2.3
1:4	9.0	10.9	3,630	1.5	1.2	3.0	12.7	3,430	2.1	0.7	1.8
1:4	9.5	12.5	3,190	1.4	1.4	3.5	12.9	3,070	1.7	.7	1.7
1:4	10.0	12.8	2,850	1.4	1.7	4.1	13.2	2,770	1.5	1.2	3.0
1:4	10.5	12.7	2,540	1.6	1.3	3.3	12.7	2,520	1.3	0.9	2.3
1:4.5	9.0	11.6	2,840	2.1	1.3	3.1	13.3	2,700	2.1	.8	2.0
1:4.5	9.5	12.6	2,460	3.0	1.3	3.3	13.3	2,430	3.0	.8	2.0
1:4.5	10.0	12.7	2,220	2.7	1.8	4.5	13.0	2,200	2.1	.8	2.1
1:4.5	10.5	12.5	2,020	2.6	2.0	4.9	13.3	1,960	3.8	1.2	2.9

* Specimen showed segregation and was not included in discussion.

TABLE 5.—*Characteristics of standard Ottawa sand (20–30) mortars compacted by two vibrators by two methods of filling molds*—Continued

Proportions by weight	Water content	Molds vibrated as filled					Molds filled, then vibrated				
		Air voids	Compressive strength	Strength dispersion			Air voids	Compressive strength	Strength dispersion		
				C_1	$\overline{C}_1$	C_i			C_1	$\overline{C}_1$	C_i
Magnetic vibrator—frequency, 120 c/s; amplitude, 0.0074 in.; acceleration, 5 *g*											
	Percent	*Percent*	*lb/in.*^{2}				*Percent*	*lb/in.*^{2}			
1:3	9.0	6.5	6,800	2.5	1.5	3.7	6.5	6,810	2.2	1.3	3.2
1:3	9.5	6.1	6,500	3.0	3.9	9.6	6.6	6,280	2.1	2.7	6.7
1:3	10.0	6.2	5,930	4.7	5.3	13.1	6.9	5,840	2.8	4.7	11.4
1:3	10.5	5.7	5,330	2.0	4.1	10.1	7.7	5,100	3.5	4.4	10.8
1:3.5	9.0	7.6	• 5,370	2.2	2.2	5.3	9.4	• 5,020	1.9	1.8	4.3
1:3.5	9.5	6.6	5,200	1.5	3.8	9.2	8.3	4,940	2.9	3.5	8.6
1:3.5	10.0	5.9	4,750	2.9	4.1	10.1	9.4	4,320	4.3	5.7	13.9
1:3.5	10.5	6.2	4,190	3.0	5.1	12.5	10.0	3,730	3.6	4.5	11.0
1:4	9.0	10.5	• 3,510	2.5	2.5	6.1	12.0	• 3,300	1.3	1.8	4.5
1:4	9.5	9.2	• 3,540	3.6	2.6	6.4	10.4	• 3,240	3.1	2.1	5.1
1:4	10.0	7.3	3,480	1.8	2.9	7.2	9.0	3,200	2.0	4.1	10.0
1:4	10.5	5.9	3,210	3.0	3.2	7.8	8.5	2,960	2.4	5.6	13.8
1:4.5	9.0	12.0	• 2,610	3.6	1.6	3.9	13.7	• 2,430	3.2	2.5	6.0
1:4.5	9.5	10.6	• 2,570	1.8	1.4	3.4	12.3	• 2,380	2.6	1.3	3.3
1:4.5	10.0	8.8	• 2,590	2.4	2.2	5.5	10.4	• 2,340	4.5	2.5	6.1
1:4.5	10.5	7.3	2,470	2.1	2.7	6.7	8.6	2,300	4.3	4.1	10.0

• Specimen showed segregation and was not included in discussion.

All cubes compacted at 83 c/s on the rotary vibrator were homogeneous and free from visible defects. Of the 32 groups compacted at 40 c/s on this vibrator, 20 showed nonuniform compaction. Of the 32 groups compacted on the magnetic vibrator, 12 had defective tops. Although this is somewhat better than the results obtained on the rotary vibrator operated at 40 c/s, it is far short of the performance of the rotary vibrator operated at 83 c/s where all specimens were homogeneously compacted. If the standard sand test mortars were completely compacted into the molds, theoretically there would be enough cement and water to completely fill the interstices in the sand only for the 1:3 mortars and the two wetter 1:35 mortars; there would be up to approximately 6.5 percent of unfilled space, or air voids, in the remaining mortars. Table 4 shows that the measured percentage of air voids after compaction on the rotary vibrator exceeded the theoretical value, and furthermore that the air voids increased with water content instead of decreasing as the theoretical values. Of the cubes compacted at 83 c/s on the rotary vibrator the air voids were with two exceptions greater than 10 percent, and, for like mortars, greater than the voids in cubes compacted on the same vibrator at 40 c/s, or compacted on the magnetic vibrator.

For the cubes compacted on the rotary vibrator at 83 c/s there was little difference in the amount of voids in the cubes made by the two methods of filling the molds, except for the 1:4.5 mortar and the driest 1:4 mortar, in which case those made by vibration during filling had somewhat lower voids.

The range of strengths obtained by the standard sand mortars of table 5 is from 1,960 to 6,810 lb/in.^{2}. For each cement:sand ratio the strength decreased with increase in water content. The strengths

increased with increase in richness in cement, the four mortars of any one richness being stronger than those of the next leaner mix, except that the wettest mortar of the richer mix had slightly less strength than the driest mortar of the next leaner mix.

The strengths obtained on the specimens made by filling the vibrating molds, 40 c/s on the rotary vibrator, or on the magnetic vibrator, have a tendency to be higher than the strengths of specimens made by vibrating after filling the molds. However, as with the air-void content, the strengths obtained on the rotary vibrator at 83 c/s were practically the same for the two methods of mold filling. The independence of the strength from the method of mold filling is of advantage in a standard test method.

The 1:4 mortar, 10 percent mixing water, compacted on the rotary vibrator at 83 c/s, gave strengths of approximately 2,800 lb/in.^{2}, that with 9.5 percent of mixing water 3,100 lb/in.^{2}. These strengths approximate that of the plastic mortar cubes of SS–C–158, and also the strengths of the representative concrete with $C/W=1.7$.

A relatively small number of groups of cubes made on the magnetic vibrator and on the rotary vibrator at 40 c/s was uniformly compacted; a satisfactory comparison of the relative reproducibility of the cubes compacted on the two vibrators and those compacted on the rotary vibrator at the two speeds could not be made. It would appear, however, that for cubes without visible defects, there is no essential difference between the strength reproducibility of cubes of any one mix and of any one water content compacted on the rotary vibrator operated at 40 and at 83 c/s. The strength dispersion of batches compacted on the magnetic vibrator was somewhat greater than that of batches compacted on the rotary vibrator. The reproducibility of the strengths of individual specimens on the rotary vibrator was far better than on the magnetic.

For cubes without segregation, there appeared to be but slight difference between the reproducibility of the cube batches, made by vibration after filling molds, over those filled during vibration.

The relation of the dispersion of individual strengths in the batch to the dispersion of the average strengths of batches is quite different for specimens compacted on the magnetic vibrator than it is for specimens compacted on the rotary vibrator. For the specimens compacted at 40 c/s on the rotary vibrator $C_b > \bar{C}_b$ for all 12 cases in which defects were not apparent. That is, the coefficient of variation of the batches was greater than it would have been if the variation of the average was due solely to the deviations of the individual cube strengths. This shows a batch-to-batch difference, which may be attributed to day-to-day variations in thoroughness of mixing, errors in proportioning, etc. In the specimens compacted at the higher speed (83 c/s), on the same vibrator, with 4 exceptions in the 32 different groups, the same characteristic prevailed, that is, $C_b > \overline{C}_b$.

On the other hand, for the 20 specimens compacted on the magnetic vibrator which had no visible defects, with 3 exceptions C_b was less than $\overline{C}_b$. This might be attributed to some cause such as strength being a function of the position of the specimen on the vibrator. If this were true, the strength of a cube would be different for each of the six possible cube positions on the vibrator. Let us assume the extreme condition where the strength of the cube, although differing

with the position, would be the same in any one of these positions from one batch to the next. Obviously the strength of the batches would then be the same, but there would be a positive and finite standard deviation C_i of the individual cubes within the batch. In this case it is apparent that $\overline{C}_b$ computed from C_i would be greater than C_b, which in this case is equal to zero.

In the tests no record was kept of the specimen location. A few batches made up to test the assumption that the strength is a function of location of the specimen on the vibrator were inconclusive, being obscured by the fact that C_b has an appreciable magnitude. It was not thought worth the effort to make the comparatively large number of batches necessary to verify or disprove the assumption.

V. SUMMARY AND CONCLUSIONS

1. Two vibrators were employed in the investigation: (1) An electromagnetic vibrator having a fixed frequency of twice the frequency of the power supply. The amplitude varied with impressed voltage and also with the table weight so that, near resonance, where it was necessary to operate in order to compact the mortars, the amplitude varied as the mortars became compacted in the molds. (2) A rotary vibrator having a circular horizontal motion in which the speed of vibration could be adjusted up to a maximum of 83 c/s. The amplitude could be adjusted with a maximum of 0.03 in. The mortars rotated in the molds during vibration. However, for all but the very driest mixes, the corners of the molds were completely filled. Studies with mortars of two colors showed that the motion did not produce internal segregation or intermixing except in specimens showing visible external segregation at the top.

2. The amount of rotation of the mortars on the rotary vibrator suggests itself as a measure of the consistency required for a mortar to be compacted by vibration, but the measurement was so tedious and subject to such experimental error that it is not recommended as a routine test method.

3. The spread of the mortar on a flat plate attached to the vibrators was observed, as a possible method for measuring consistency. The outline of the spread mortar on the rotary vibrator was too irregular to warrant further consideration of the method on this vibrator.

4. The flow of wet mortars on the standard flow table is consistent, but that of the dry mixes erratic. A V-trough was designed for use with the rotary and also the magnetic vibrator, to measure the flows of dry mortars. This trough on the rotary vibrator was found to differentiate between the flows of dry mortars. Therefore, the V-trough may be used to measure the consistency of the drier mixes suitable for compaction by vibration, and the flow table for the wetter or "plastic" mixes.

5. Standard (20–30) Ottawa sand mortars appeared to have some desirable properties not found with other mixes for compaction by vibration, such as simplicity of proportioning and greater reproducibility of strength.

6. In standard Ottawa sand specimens compacted by vibrating from 20 to 90 sec on the rotary vibrator at 33 to 83 c/s, little strength was gained by vibrating longer than 40 sec, although the greatest

strength was obtained in all cases by vibrating 90 sec. The strength increased as the frequency of vibration increased, but in progressively smaller steps.

7. Standard Ottawa sand mortars with proportions ranging from 1:3 to 1:4.5, with water contents of 9 to 10.5 percent, were compacted on each of the vibrators. The results of these tests may be summarized as follows:

a. All specimens made on the rotary vibrator at 83 c/s were apparently uniformly compacted. The drier and the leaner mixes when compacted on the magnetic vibrator or on the rotary vibrator at 40 c/s had defective upper portions.

b. The batch strength reproducibility of batches of the 1:3.5 and 1:4 mortars compacted on the rotary vibrator at 83 c/s was better than that of the 1:3 and 1:4.5 mortars. The average coefficient of variation (C_b) of the strengths of the 1:3.5 and 1:4 mortars was approximately 1.5 percent, compared with 3.8 percent for the hand-compacted specimens made according to Federal Specification SS–C–158. The reproducibility of the specimens compacted on the rotary vibrator at 83 c/s was in most cases superior to that of similar specimens compacted on the magnetic vibrator or the rotary vibrator at 40 c/s.

c. The strengths of the 1:4 standard Ottawa sand mortar, 9.5 and 10 percent mixing water, compacted on the rotary vibrator at 83 c/s were approximately 3,100 and 2,800 lb/in.^{2}, respectively. The strength of "plastic" mortar specimens hand-fabricated in accordance with Federal Specification SS–C–158 was 2,900 lb/in.^{2} This is approximating the strength of a 1:2.2:3.8 concrete of the same cement and with a C/W ratio of 1.7.

8. With few exceptions, the reproducibility of batches of mixes with all combinations of aggregates tested compacted on the rotary vibrator was superior to that of standard hand-compacted batches. In the mixes most suitable for vibration, the batch variation was less than half that of the hand-compacted specimens made of fine testing sand.

VI. REFERENCES

[1] William A. Blanchette, *Some new relations bearing on concrete mixtures*, Public Roads **15,** 57 (May 1934).

[2] W. H. Glanville, and D. A. G. Reid, *Mortar tests as a guide to the strength of concrete*, Structural Eng. **12,** 242 (1934).

[3] W. H. Glanville, *Strength tests for cement*, Structural Engr. (London) **15,** 50 (1937).

[4] W. Edwards Deming, and Raymond T. Birge, Rev. Mod. Phys. **6,** 119 (1934).

Washington, June 19, 1939.

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RESEARCH PAPER RP1274

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ALPHA AND BETA METHYL LYXOSIDES, MANNOSIDES, GULOSIDES, AND HEPTOSIDES OF LIKE CONFIGURATION[1]

By Horace S. Isbell and Harriet L. Frush

ABSTRACT

Eleven new sugar derivatives and numerous optical rotation and hydrolysis measurements are reported. A comparison of the alpha and beta methyl glucosides, mannosides, galactosides, and gulosides shows that the configurations of all of the asymmetric carbons in the pyranose ring affect the rate of hydrolysis, and that there is no fixed relationship between the configuration of the glycosidic carbon and the relative rates for the hydrolysis of the alpha and beta modifications. The configuration of carbon 3 appears to influence markedly the relative rates for the hydrolysis of the alpha and beta modifications. Aldo-pyranosides having *trans* configurations for carbons 1 and 3 are hydrolyzed more slowly than the corresponding modifications having *cis* configurations for carbons 1 and 3. This unexpectedly large influence of carbon 3, and the close resemblance of each pentose to the corresponding hexose which has the *trans* configuration for carbons 3 and 5 are discussed in relation to the spacial arrangement of the whole molecule. The similarity of the methyl gulosides and α-glucoheptosides on the one hand, and the methyl lyxosides, mannosides, and α-galaheptosides on the other hand, furnishes a substantial basis for the allocation of lyxose to the mannose series.

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[1] This paper was read before the Division of Sugar Chemistry and Technology of the American Chemical Society at Baltimore, Md., April 1939.

I. STRUCTURAL AND CONFIGURATIONAL RELATIONSHIPS FOR THE PENTOSES, HEXOSES, AND HEPTOSES

In previous publications [1, 2, 3],[2] the similarity of substances which have like configurations for the five carbons comprising the pyranose ring has been stressed. The object of the present investigation was to provide additional information to correlate sugars having like configuration for atoms comprising the pyranose ring and to determine to what extent the properties of the glycosides depend on the configurations of the several asymmetric carbons of the pyranose ring. In the pyranose series, the different configurations for the first carbon give rise to the alpha and beta isomers, while the different configurations for carbons 2, 3, 4, and 5 give rise to the various sugars. These sugars may be considered in eight groups, according to whether their ring configuration corresponds to that of glucose, mannose, galactose, talose, gulose, idose, allose, or altrose. The heptoses and higher sugars differ from the hexoses merely in the number and in the stereoisomeric arrangement of the atoms in the side chain, while the pentoses differ from the hexoses in that the CH_2OH group is replaced by hydrogen. Since the fifth carbon is not asymmetric in the pentose series, each pentose is configurationally related to two hexoses, which differ in the arrangement of the groups attached to carbon 5. Thus *d*-xylose is related to *d*-glucose and *l*-idose; *l*-arabinose is related to *d*-galactose and *l*-altrose; *d*-lyxose is related to *d*-mannose and *l*-gulose; and *l*-ribose is related to *d*-talose and *l*-allose. These relationships are illustrated by the accompanying projectional formulas. The marked resemblance in the properties of xylose and arabinose to those of glucose and galactose, respectively, has been shown by much experimental work and noted by numerous investigators. In order to account for this resemblance, one of us suggested that the pentose molecule as a whole is dissymmetric, and that the pyranose ring in *l*-arabinose for some reason takes a form which resembles a *d*-galactose ring [1, 2], and that the pyranose rings of *d*-xylose, *d*-lyxose, and *l*-ribose, respectively resemble the rings of *d*-glucose, *d*-mannose, and *d*-talose more closely than they resemble the rings of *l*-idose, *l*-gulose, and *l*-allose. The classification of *l*-arabinose with *d*-galactose and of *d*-xylose with *d*-glucose is supported by considerable experimental work, but since relatively few data were available for lyxose and ribose, an investigation of substances configurationally related to lyxose and ribose was begun in this laboratory.

A survey of the literature concerning the methyl glycopyranosides of the lyxose, mannose, and gulose series reveals that the glycosides configurationally related to α-methyl *d*-lyxoside (or the mirror images in the case of the heptosides and gulosides) have been crystallized and their properties studied, while the glycosides configurationally related to β-methyl *d*-lyxoside, with the exception of α-methyl *d*-guloside, have not been crystallized. Inasmuch as some of these compounds have been considered key substances in the problems of sugar structure, their crystallization has been attempted by a number of previous workers, but without success. In the course of this investigation we have prepared a series of methyl glycosides having the methyl lyxoside structure so that we have for comparison the α- and β-methyl *d*-lyxosides, *d*-mannosides, *d*-gulosides, *d*-α-galaheptosides, and *d*-α-gluco-

[2] Figures in brackets indicate the literature references at the end of this paper.

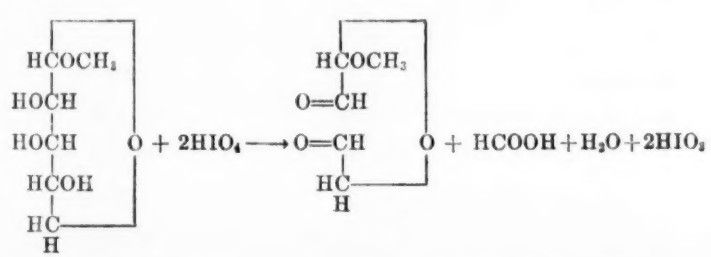
heptosides. Nine of these compounds were obtained in the crystalline state, while β-methyl *d*-α-galaheptoside was prepared as a pure sirup. The heretofore unknown β-methyl *d*-lyxoside was crystallized from the mother liquor which remained after the preparation of α-methyl *d*-lyxoside by Fischer's hydrogen chloride method. β-Methyl *d*-mannoside was obtained as a crystalline isopropyl alcoholate, while α-methyl *d*-α-glucoheptoside was crystallized through the intermediate use of a crystalline calcium compound by the process originated by Isbell [4] for the preparation of the methyl gulosides. The tendency of the members of the lyxose, mannose, and gulose series to form crystalline calcium chloride compounds was shown further by the preparation of crystalline calcium chloride compounds of α-methyl *d*-lyxoside, β-methyl *d*-α-glucoheptoside, and β-methyl *d*-mannoside. Several of the glycosides were separated as acetates, which were deacetylated by Isbell's barium methylate method [5]. The new compounds are listed in table 1.

TABLE 1.—*New compounds prepared in this investigation*

Substance	Experimental results		Solvent	Concentration	Formula
	Melting point	Specific rotation $[\alpha]_D^{20}$			
	°C			Percent	
β-Methyl *d*-lyxopyranoside	118	−128.1	H_2O	2.5	$C_6H_{12}O_5$
β-Methyl triacetyl-*d*-lyxopyranoside	88 to 89	−109.5	$CHCl_3$	4.5	$C_{12}H_{18}O_8$
β-Methyl *d*-mannopyranoside	(a)	−69.8	H_2O	3	$C_7H_{14}O_6$
β-Methyl *d*-mannopyranoside.C_3H_8O	74 to 75	−53.3	H_2O	4	$C_{10}H_{22}O_7$
α-Methyl *d*-α-glucoheptopyranoside	106 to 107	+111.5	H_2O	4	$C_8H_{16}O_7$
α-Methyl penta-acetyl-*d*-α-glucoheptopyranoside.	174 to 175	+107.4	$CHCl_3$	1	$C_{18}H_{26}O_{12}$
β-Methyl *d*-α-galaheptopyranoside	(a)	+74	H_2O	2.8	$C_8H_{16}O_7$
β-Methyl penta-acetyl-*d*-α-galaheptopyranoside.	171 to 173	+77.6	$CHCl_3$	4	$C_{18}H_{26}O_{12}$
α-Methyl *d*-β-galaheptopyranoside	154 to 155	−108	H_2O	4	$C_8H_{16}O_7$
α-Methyl *d*-lyxopyranoside.$CaCl_2$. $2H_2O$.		+31.2	H_2O	5	$C_6H_{12}O_5.CaCl_2.2H_2O$
α-Methyl *d*-α-glucoheptopyranoside. $CaCl_2.H_2O$.		+69.1	H_2O	4	$C_8H_{16}O_7.CaCl_2.H_2O$
(β-Methyl *d*-α-glucoheptopyranoside)$_2$.$CaCl_2.2H_2O$.		−56.1	H_2O	4	$(C_8H_{16}O_7)_2.CaCl_2.2H_2O$

a Sirup.

The structure of our new β-methyl *d*-lyxoside was determined by the application of the periodic oxidation method of Jackson and Hudson [6]. As shown by Maclay and Hudson [7], α-methyl *d*-lyxopyranoside is oxidized by periodic acid according to the following equation:

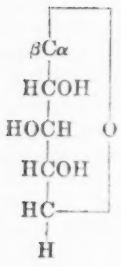


α-Methyl *d*-lyxopyranoside *d*-Methoxy-diglycolic aldehyde

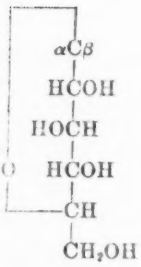
FORMULAS FOR CONFIGURATIONALLY RELATED SUBSTANCES[1]

d-Glucose

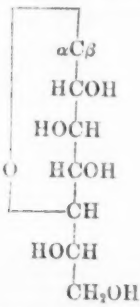
l-β-Galaheptose



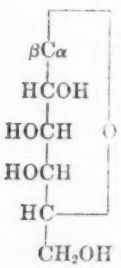
d-Xylose



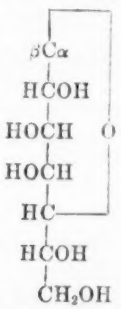
l-Idose



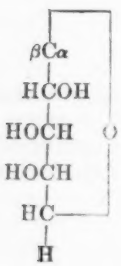
l-β-Glucoheptose



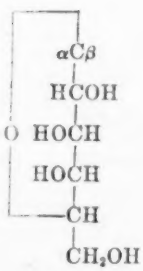
d-Galactose



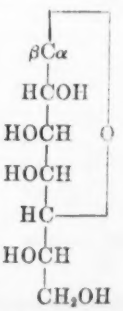
d-α-Mannoheptose



l-Arabinose



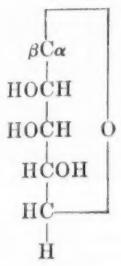
l-Altrose



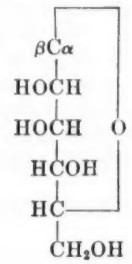
d-β-Guloheptose

[1] In the alpha modification the functional group (OH, CH_2O, etc.) lies in the position represented by alpha, with a hydrogen atom saturating the remaining valence of the carbon atom. In the beta modification, the functional group lies in the position represented by beta.

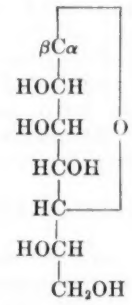
FORMULAS FOR CONFIGURATIONALLY RELATED SUBSTANCES—Continued



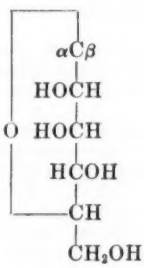
d-Lyxose



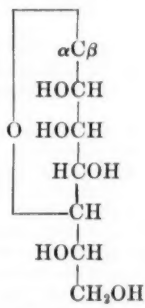
d-Mannose



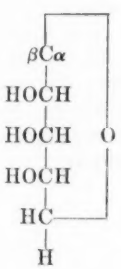
l-α-Galaheptose



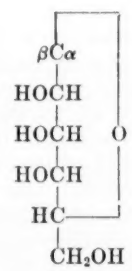
l-Gulose



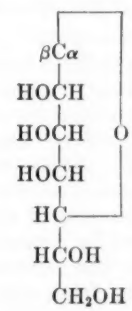
l-α-Glucoheptose



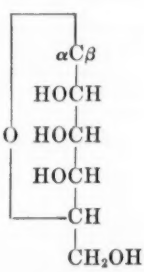
l-Ribose



d-Talose



d-β-Mannoheptose



l-Allose

l-α-Guloheptose

From the results reported by Jackson and Hudson, one would expect β-methyl *d*-lyxoside to follow the same course as α-methyl *d*-lyxopyranoside and to give *l*-methoxy-diglycolic aldehyde instead of *d*-methoxy-diglycolic aldehyde. We found experimentally that β-methyl *d*-lyxoside reacts with 2 moles of periodic acid, and that the optical rotation of the reaction product differs merely in sign from that obtained with α-methyl *d*-lyxopyranoside. This proves that β-methyl *d*-lyxoside is a pyranoside and that it has the same configuration for carbon 1 as β-methyl *d*-glucopyranoside.

II. RATES OF HYDROLYSIS FOR THE METHYL GLYCOSIDES

In a brilliant contribution over 35 years ago, Armstrong [8] wrote the following passage:

> It will be noticed that the various hexosides vary widely in stability: the β-glucosides undergoing hydrolysis more rapidly than the stereoisomeric α-compounds whilst the galactosides are more rapidly attacked than the corresponding glucosides.
>
> In the case of the α- and β-glucosides and galactosides, the stereoisomerism in each pair of compounds is confined to the terminal carbon atom; it is, perhaps, noteworthy that there should be so considerable a difference between compounds so related.
>
> But it is even more surprising that a change in the general configuration at the fourth carbon atom, affecting only the nature of the attachment of the oxygen atoms within the ring, such as occurs when glucose passes into galactose, should have so marked an influence on the activity of the group associated with the terminal carbon atom. Such a result enhances the probability of the conclusion that the active system within which the change takes place is formed by the association of acid-water molecules with the oxygen atom in the pentaphane ring; in other words, that this oxygen atom is the attractive center.
>
> The argument here made use of renders it desirable that the behavior of the isomeric mannosides towards acids should also be studied in order that it may be possible eventually to define more or less accurately the functions of the different oxygen atoms in the molecule.

In subsequent years the glycosides of glucose, mannose, and galactose have been investigated, but very little work has been done on the glycosides of gulose, idose, allose, altrose, and talose. Before extensive conclusions can be drawn as to the relationships between the configurations and the relative reactivity, it will be necessary to investigate glycosides of all eight pyranose types at several temperatures and concentrations. However, the velocity constants measured in the course of this investigation (table 2) in conjunction with those reported by Armstrong [8] and by Riiber and Sørensen [9] (see table 3) provide the necessary information for comparing a series of glycosides differing from one another in the configurations of each of the five carbons comprising the pyranose ring. The velocity constants used for the comparisons which follow are given in tables 2 and 3.

TABLE 2.—*Velocity constants*

Substance	0.05 *N* HCl at 98° C	0.5 *N* HCl [1] at 75° C
α-Methyl *d*-lyxopyranoside	0.00374	0.00286
β-Methyl *d*-lyxopyranoside	.0135	
α-Methyl *d*-mannopyranoside	.00069	.000471
β-Methyl *d*-mannopyranoside (isopropyl alcoholate)	.00167	.00113
α-Methyl *d*-gulopyranoside (hydrate)	.0125	.0115
β-Methyl *d*-gulopyranoside	.00576	.00377
α-Methyl *d*-α-glucoheptopyranoside	.00486	.00417
β-Methyl *d*-α-glucoheptopyranoside	.00219	.00132
α-Methyl *d*-α-galaheptopyranoside	.000381	
β-Methyl *d*-α-galaheptopyranoside	.000860	
α-Methyl *d*-β-galaheptopyranoside	.000166	

[1] The measurements were made as described on page 149. The velocity constants were calculated from the equation for a first-order reaction and are expressed in Briggs logarithms and in minutes.

TABLE 3.—*Velocity constants reported by Riiber and Sørensen [11]*

Substance	Velocity constants [1]		Reference
	0.01 *N* HCl at 100° C	0.5 *N* HCl at 75° C	
α-Methyl glucopyranoside	0.000066	0.000198	[8]
β-Methyl glucopyranoside	.000137	.000379	[8]
α-Methyl xylopyranoside		.00090	[9]
β-Methyl xylopyranoside		.0018	[9]
α-Methyl galactopyranoside		.00104	[8]
β-Methyl galactopyranoside		.00183	[8]
α-Methyl arabinopyranoside		.0018	[9]
β-Methyl arabinopyranoside		.0026	[9]
α-Methyl rhamnopyranoside	.00055		[9]
β-Methyl rhamnopyranoside	.00125		[9]
α-Methyl mannopyranoside	.000137		[9]
β-Methyl mannopyranoside	.00021		[10]

[1] The velocity constants were calculated from the equation for a first-order reaction and are expressed in Briggs logarithms and in minutes.

TABLE 4.—*Effect of configuration on rate of hydrolysis of the hexopyranosides*

[0.5 *N* HCl at 75° C]

Substances differing on—	Substances	*k*/*k'*
Carbon 1	β-Methyl *d*-glucoside:α-methyl *d*-glucoside	1.91
	β-Methyl *d*-mannoside:α-methyl *d*-mannoside	2.40
	β-Methyl *d*-galactoside:α-methyl *d*-galactoside	1.76
	β-Methyl *d*-guloside:α-methyl *d*-guloside	0.33
Carbon 2	α-Methyl *d*-mannoside:α-methyl *d*-glucoside	2.38
	β-Methyl *d*-mannoside:β-methyl *d*-glucoside	2.98
Carbon 3	α-Methyl *d*-guloside:α-methyl *d*-galactoside	11.06
	β-Methyl *d*-guloside:β-methyl *d*-galactoside	2.06
Carbon 4	α-Methyl *d*-galactoside:α-methyl *d*-glucoside	5.25
	β-Methyl *d*-galactoside:β-methyl *d*-glucoside	4.83
Carbon 5	α-Methyl *l*-guloside [1]:β-methyl *d*-mannoside	10.18
	β-Methyl *l*-guloside [1]:α-methyl *d*-mannoside	8.00

[1] Measurement made on enantiomorphic substance.

TABLE 5.—*Effect of the configuration of carbon 3 on the rates of hydrolysis of the alpha and beta modifications of the methyl glycopyranosides*

Substance	Velocity constants (0.05 *N* HCl at 98° to 100° C)		$\frac{k_{trans}}{k_{cis}}$	Velocity constants (0.5 *N* HCl at 75° C)		$\frac{k_{trans}}{k_{cis}}$
	Cis modification on carbons 1 and 3	*Trans* modification on carbons 1 and 3		*Cis* modification on carbons 1 and 3	*Trans* modification on carbons 1 and 3	
Methyl *d*-glucopyranosides				0.000379	0.000198	0.52
Methyl *d*-xylopyranosides				.0018	.00090	.50
Methyl *d*-galactopyranosides				.00183	.00104	.57
Methyl *l*-arabinopyranosides				.0026	.0018	.69
Methyl *d*-mannopyranosides	0.00167	0.00069	0.41	.00113	.000471	.42
Methyl *d*-lyxopyranosides	.0135	.00374	.28			
Methyl *d*-α-galaheptopyranosides	.000860	.000381	.44			
Methyl *d*-gulopyranosides	.0125	.00576	.46	.0115	.00377	.33
Methyl *d*-α-glucoheptopyranosides	.00486	.00219	.45	.00417	.00132	.32

Previous investigators have shown that the beta methyl *d*-glucosides, *d*-mannosides, *d*-galactosides, *d*-xylosides, and *l*-arabinosides are hydrolyzed slightly more rapidly than the corresponding alpha isomers. From these results the concept arose that all beta glycosides are hydrolyzed more rapidly than the corresponding alpha glycosides, although the earlier work was based on only three of the eight pyranose types (glucose, galactose, and mannose). In this investigation we have extended the work to include the gulose pyranose type. Much to our surprise, α-methyl *d*-guloside and α-methyl *d*-α-glucoheptoside, which has the α-methyl *d*-guloside structure, were found to be hydrolyzed more rapidly than the corresponding beta isomers. It may be observed from the ratios given in table 4 that the alpha and beta glycosides of the same sugar usually differ less in rate of hydrolysis than do the glycosides of the separate sugars. In other words, the configuration of the first carbon is not the principal factor for determining the rate of hydrolysis. This is in marked contrast to the results obtained by the oxidation of the free sugars with bromine water, in which process the configuration of the first carbon is the predominating factor for determining the rate of the reaction [1, 2]. Since the mannosides differ from the glucosides in the configuration of carbon 2, the effect of the configuration of this carbon on the rates of hydrolysis is shown by comparing the methyl *d*-mannosides with the methyl *d*-glucosides. Likewise, the effect of the configurations of carbons 3, 4, and 5 is shown by comparing the methyl *d*-gulosides with the *d*-galactosides, methyl *d*-galactosides with the *d*-glucosides, and the methyl *l*-gulosides with the *d*-mannosides. The results of such comparisons clearly show that the configurations of carbons 2, 3, 4, and 5 separately and jointly affect the rate of hydrolysis. The configuration of carbon 5 appears to be particularly important in relation to the rate of hydrolysis. Also, the relationship between the configuration of carbon 3 and the rates of hydrolysis for the alpha and beta modifications is noteworthy. As may be observed by comparison of the projectional formulas with the relative rates of hydrolysis given in table 5, the modifications of the methyl pyranosides which have *trans* configurations for carbons 1 and 3 are hydrolyzed more

slowly than the corresponding modifications which have *cis* configurations.[3] That is, reversing the configuration of carbon 3 in the galactose series to give substances in the gulose series results in a change in the relative stability of the alpha and beta isomers towards acid hydrolysis. As may be noted from a space model, carbon 3 lies opposite the oxygen of the ring and its attached groups appear to be in a particularly favorable position to influence the conformation of the ring. Perhaps this accounts for the unexpectedly large influence of the configuration of carbon 3 on the relative reactivities of the alpha and beta modifications. Another observation, which may depend on the effect of the configuration of carbon 3, is that in the pentose series where the ring-forming carbon is not asymmetric, each pentose resembles the hexose in which carbons 3 and 5 have opposite configurations.

TABLE 6.—*Effect of the group R, attached to carbon 5, on the rates of hydrolysis for methyl pyranosides* [1]

Substance	Heptoside		Hexoside		Methyl pentoside		Pentoside	
	R=CH(OH)CH_2OH	Relative rate [2]	R=CH_2OH	Relative rate [2]	R=CH_3	Relative rate [2]	R=H	Relative rate [2]
α-Methyl	α-Galaheptoside*	0.55	Mannoside	1	Rhamnoside*	4.01	Lyxoside	6.07
β-Methyl	do.*	.51	do	1	do.*	5.95	do.*	8.08
α-Methyl	β-Galaheptoside*	3.50	Glucoside	1			Xyloside	4.55
β-Methyl			do	1			do	4.75
α-Methyl			Galactoside	1			Arabinoside	1.73
β-Methyl			do	1			do	1.42
α-Methyl	α-Glucoheptoside	.36	Guloside	1			Lyxoside [4*]	1.08
β-Methyl	do	.35	do	1			do.[5*]	0.65

[1] The results are based on comparable measurements at 75° C with the exception of those marked with an asterisk, which are based on comparable measurements at either 98° or 100° C.
[2] The velocity constant for the hydrolysis of the glycoside divided by the velocity constant of the configurationally related hexosides under like conditions.
[3] Since the measurements for α-methyl *d*-glucoside and α-methyl *d*-β-galaheptoside were made in 0.01 *N* and in 0.05 *N* HCl, respectively, the velocity constants were reduced to a comparable basis by use of the relative activity of the two solutions as estimated from the rates of hydrolysis of α-methyl *d*-mannoside.
[4] β-Methyl lyxoside is compared with α-methyl guloside, to which it is configurationally related.
[5] α-Methyl lyxoside is compared with β-methyl guloside, to which it is configurationally related.

As noted by Riiber and Sørensen [9], the methyl pentosides are hydrolyzed more rapidly than the methyl hexosides. Our comparisons, given in table 6, show that the methyl arabinosides are hydrolyzed about 1½ times as rapidly as the methyl galactosides and that the xylosides are hydrolyzed about 5 times as rapidly as the glucosides. Judging from these values, one would expect the lyxosides to be hydrolyzed considerably more rapidly than the configurationally related hexosides. Our experimental results reveal that the lyxosides are hydrolyzed on the average about 7 times as rapidly as the mannosides and only eight-tenths as rapidly as the gulosides. Since the rhamnosides are hydrolyzed about 5 times as rapidly as the configurationally related mannosides, the comparisons clearly indicate that the lyxosides should be classified in the mannose series. The classification of the lyxosides in the mannose series is supported by their optical rotations, which are discussed in the next section of this paper.

[3] This generalization is based on data which include four of the eight pyranose types. Obviously, it would be of interest to ascertain whether this relationship between rate of hydrolysis and configuration also applies to glycosides having the allose, altrose, idose, and talose configurations.

III. COMPARISON OF MOLECULAR ROTATIONS

1. ROTATIONAL DIFFERENCE FOR THE ALPHA AND BETA ISOMERS

The optical rotations of our new compounds, in conjunction with values to be found in the literature, provide data for many interesting comparisons. In making the comparisons which follow, the numerical values for the optical rotations recorded in table 7 were used.

A comparison of the optical rotations provides a simple and convenient method for the correlation of the alpha and beta methyl pentosides with the configurationally related methyl hexosides. If the molecular rotations of the alpha and beta modifications be considered as $+A+B$ and $-A+B$, the difference in the molecular rotations is Hudson's $2A$ [4] [11]. As may be observed from the data given in table 8, the difference in the molecular rotations of the α- and β-methyl *d*-lyxosides (+30,800) agrees more closely with the differences found for the methyl *d*-mannosides (+28,900) and *d*-α-galaheptosides (+32,300) than with the differences found for the methyl *d*-gulosides (+39,400) and *d*-α-glucoheptosides (+41,800). A similar relationship is apparent in the differences for the corresponding acetylated glycosides. As pointed out more fully on page 147, the α-methyl penta-acetyl-*d*-α-glucoheptoside prepared by us differs in optical rotation and melting point from that prepared by Haworth, Hirst, and Stacey [12]. Possibly one of the compounds is not pure, but it is noteworthy that the value of $2A$ (+53,600) for the acetylated *d*-α-glucoheptosides obtained by using the rotation of our α-methyl penta-acetyl-*d*-α-glucoheptoside agrees with the values obtained for the acetylated methyl *d*-glucosides (+53,900), *d*-xylosides (+52,400), and *d*-galactosides (+53,100). The value (+46,500) obtained by using the rotation of Haworth, Hirst, and Stacey's α-methyl penta-acetyl-*d*-α-glucoheptoside agrees with the value obtained from the acetylated methyl *d*-gulosides (+46,900). Probably the agreements in the values just noted are accidental, but possibly the two α-methyl penta-acetyl-*d*-α-glucoheptosides are definite compounds which differ in the conformation of the ring, or in some other unknown manner. One of these compounds may be structurally analogous to the acetylated methyl *d*-glucoside, while the other may be analogous to the acetylated methyl *d*-guloside. These compounds may comprise a pair of substances differing in ring conformation, such as the strainless ring isomers first mentioned by Haworth in 1929 [13], and suggested by Isbell in 1937 [1] as an explanation for the differences in the optical rotational relationships in the mannose and glucose series. More recently other investigators have recognized the possibility of different ring conformations for the pyranoid ring [14, 15].

[4] If the value of $2A$ is obtained by subtracting the molecular rotation of the glycoside having the methoxyl group on the left (in the Fischer projectional formula) from the rotation of the modification which differs by having the glycosidic methoxyl on the right, the value of $2A$ is positive for all known alpha-beta pairs.

TABLE 7.—*Optical rotations used for the comparison of the molecular rotations*

	α-Modification			β-Modification		
	$[\alpha]_D^{20}$	$[M]$ Initial	Reference	$[\alpha]_D^{20}$	$[M]$ Initial	Reference
SUGARS						
l-Arabinose	+190.6	+28,610	[2]	[1]+34.7	+11,560	[2]
l-Ribose				+20.3	+3,050	[2]
d-Xylose	+93.6	+14,050	[2]	−20	−3,000	[16]
d-Lyxose	+5.6	+840	[2]	−72.6	−10,900	[2]
d-Glucose	+112.2	+20,210	[2]	+18.7	+3,370	[2]
d-Mannose	+29.3	+5,280	[2]	−17.0	−3,060	[2]
d-Galactose	+150.7	+27,150	[2]	+52.8	+9,510	[2]
d-Talose	+68.0	+12,250	[2, 17]	+13.2	+2,380	[2, 17]
l-Allose				−1.90	−350	[18]
l-Altrose				−28.75	−5,180	[18]
d-Gulose	+61.6	+11,100	[19]			
d-α-Glucoheptose				−28.7	−6,030	[1]
d-β-Glucoheptose				−0.1	−20	[1, 20]
d-α-Galaheptose	[2]−25.2	−5,750	[1]			
d-β-Galaheptose				−19.2	−4,040	[1]
d-α-Mannoheptose	[2]+120.0	+27,380	[1]			
d-β-Mannoheptose	[2]+45.7	+10,430	[21]			
d-α-Guloheptose	−45.7	−9,600	[22]			
d-β-Guloheptose	−120.5	−25,330	[1]			
GLYCOSIDES						
Methyl *l*-arabinosides	+245.5	+40,300	[23]	+17.3	+2,840	[23]
Methyl *d*-xylosides	+153.9	+25,260	[23]	−65.5	−10,750	[23]
Methyl *d*-lyxosides	+59.4	+9,750	[24]	−128.1	−21,030	[New]
Methyl *d*-glucosides	+158.9	+30,860	[25]	−34.2	−6,640	[25]
Methyl *d*-mannosides	+79.2	+15,380	[26]	[3]−53.3	−13,550	[New]
Methyl *d*-galactosides	+196.6	+38,180	[27]	0	0	[28]
Methyl *d*-gulosides	[2]+109.4	+23,210	[4]	−83.3	−16,180	[4]
Methyl *d*-α-glucoheptosides	+111.5	+25,000	[New]	−74.9	−16,800	[28]
Methyl *d*-α-galaheptosides	−70.2	−15,700	[29]	[4]+74	+16,600	[New]
Methyl *d*-β-galaheptosides	−108	−24,200	[New]	+36.0	+8,100	[30]
ACETYLATED GLYCOSIDES						
Methyl triacetyl-*d*-xylosides	+119.6	+34,720	[31]	−60.8	−17,650	[32]
Methyl triacetyl-*d*-lyxosides	+30.1	+8,740	[33]	−109.5	−31,780	[New]
Methyl tetra-acetyl-*d*-glucosides	+130.5	+47,280	[34]	−18.2	−6,590	[34]
Methyl tetra-acetyl-*d*-mannosides	+49.1	+17,790	[35]	−50.4	−18,260	[35]
Methyl tetra-acetyl-*d*-galactosides	+132.5	+48,000	[36]	−14.0	−5,070	[37]
Methyl tetra-acetyl-*d*-gulosides	+97.3	+35,250	[4]	−32.1	−11,630	[4]
Methyl penta-acetyl-*d*-α-glucoheptosides	+107.4	+46,650	[New]	−16	−6,950	[12]
Methyl penta-acetyl-*d*-α-glucoheptoside (Haworth)	+91	+39,500	[14]			
Methyl penta-acetyl-*d*-α-galaheptosides	−20.4	−8,860	[29]	+77.6	+33,700	[New]

[1] Rotation of β-*l*-arabinose.$CaCl_2.4H_2O$.
[2] Rotation of hydrate.
[3] Rotation of β-methyl *d*-mannoside isopropyl alcoholate.
[4] Rotation of sirup.

TABLE 8.—*Difference in the molecular rotations of the alpha and beta isomers*

Substance	Differences in the molecular rotations $(+A+B)-(-A+B)=2A$					
	Sugars		Methyl glycosides		Acetylated glycosides	
	$2A$	Reference [1]	$2A$	Reference [1]	$2A$	Reference [1]
d-Lyxose	+11,700	[38]	[2]+30,800		[2]+40,500	
d-Mannose	+8,300	[10]	[2]+28,900		+36,100	[39]
d-α-Galaheptose			[2]+32,300		[2]+42,600	
d-Gulose			+39,400	[4]	+46,900	[4]
d-α-Glucoheptose			[2]+41,800		+53,600	
d-α-Glucoheptose (Haworth, Hirst, and Stacey)					+46,500	[12]
d-Glucose	+16,800	[11]	+37,500	[11]	+53,900	[31]
d-Xylose			+36,000	[11]	+52,400	[31]
d-Galactose	+17,600	[11]	+38,200	[11]	+53,100	[31]

[1] Some of the values given in this table are based on more recent optical measurements (table 7) than the original values given in the references cited.
[2] Values calculated for the first time from optical rotations of new compounds reported in this paper.

2. COMPARISONS OF THE MOLECULAR ROTATIONS OF EPIMERIC SUBSTANCES

If the molecular rotations of two epimeric substances are $(B+R_2)$ and $(B-R_2)$, the difference in the molecular rotations is $2R_2$, which Hudson has called the "epimeric difference" [40]. The value of $2R_2$ is obtained by subtracting the molecular rotation of the substance having the hydroxyl of the second carbon on the left (in the Fischer projectional formula) from the molecular rotation of the substance which differs by having the hydroxyl of the second carbon on the right. The value for the rotation at carbon 2 is influenced by the configurations of the adjacent carbon atoms [41]. There are four possible arrangements for the adjacent carbon atoms 1 and 3:

Group 1. Hydroxyl of carbon 3 *trans* to an α hydroxyl on carbon 1.

Group 2. Hydroxyl of carbon 3 *cis* to a β hydroxyl on carbon 1.

Group 3. Hydroxyl of carbon 3 *trans* to a β hydroxyl on carbon 1.

Group 4. Hydroxyl of carbon 3 *cis* to an α hydroxyl on carbon 1.

As shown by comparisons in table 9, the members of group 1 give epimeric differences of approximately +1,500; the members of group 2 give about +8,000; and the members of group 3 give about +5,000. Data are not available for calculating epimeric differences for substances of group 4. This group would be represented by α-allose and α-altrose, or by α-gulose and α-idose. The epimeric differences for the glycosides do not differ greatly from those for the free sugars, but differ considerably from the epimeric differences found for the acetylated glycosides.

TABLE 9.—*Differences in the molecular rotations of epimeric sugars, glycosides and acetylated methyl glycosides* [1]

Epimeric differences. $(B+R_2)-(B-R_2)=2R_2$	Sugars. $2R_2$	Methyl glycosides. $2R_2$	Acetylated methyl glycosides. $2R_2$
GROUP 1			
α-*d*-Glucose—α-*d*-mannose	+14,900	+15,500	+29,500
α-*d*-Galactose—α-*d*-talose	+14,900		
α-*d*-Xylose—α-*d*-lyxose	+13,200	+15,500	+26,000
α-*d*-α-Mannoheptose—α-*d*-β-mannoheptose	+17,000		
α-*d*-α-Guloheptose—α-*d*-β-guloheptose	+15,700		
GROUP 2			
β-*d*-Glucose—β-*d*-mannose	+6,400	+6,900	+11,700
β-*d*-Galactose—β-*d*-talose	+7,100		
β-*d*-Xylose—β-*d*-lyxose	+7,900	+10,300	+14,100
β-*d*-α-Galaheptose—β-*d*-β-galaheptose		+8,500	
β-*l*-Arabinose—β-*l*-ribose	+8,500		
GROUP 3			
β-*d*-α-Glucoheptose—β-*d*-β-glucoheptose	−6,000		
β-*l*-Altrose—β-*l*-allose	−4,800		

[1] Calculated from the data given in table 7.

The relationships between the configurations and the epimeric differences just noted can be used for the classification of configurationally related substances. The similarity of the epimeric difference (+13,200) obtained from the rotations of α-*d*-xylose and α-*d*-lyxose to the epimeric difference (+14,900) obtained from α-*d*-glucose and α-*d*-mannose is evidence that α-*d*-xylose and α-*d*-lyxose differ in the same manner as α-*d*-glucose and α-*d*-mannose. The similarity of the epimeric difference (+7,900) from β-*d*-xylose and β-*d*-lyxose to the epimeric difference (+6,400) from β-*d*-glucose and β-*d*-mannose is evidence that β-*d*-xylose and β-*d*-lyxose differ in the same manner as β-*d*-glucose, and β-*d*-mannose. The similarity of the epimeric difference (+8,500) from β-*l*-arabinose and β-*l*-ribose to the epimeric difference (+7,100) from β-*d*-galactose and β-*d*-talose is evidence that β-*l*-arabinose and β-*l*-ribose differ in the same manner as β-*d*-galactose and β-*d*-talose. That is, the epimeric differences for *d*-xylose and *d*-lyxose, and for *l*-arabinose and *l*-ribose show a correlation with the epimeric differences for *d*-glucose and *d*-mannose, and for *d*-galactose and *d*-talose. It is of further interest to compare the epimeric differences obtained for the pentoses with those obtained for substances having the opposite configuration for carbon 5. As may be observed from the formulas, *l*-idose, *l*-altrose, *l*-gulose, and *l*-allose differ in the configuration of carbon 5 from the previously compared hexoses, *d*-glucose, *d*-galactose, *d*-mannose, and *d*-talose. Thus the epimeric pair, *l*-gulose and *l*-idose differ from the glucose mannose pair only in the configuration of carbon 5. Unfortunately the optical rotations of *l*-idose and *l*-gulose are not known, but the optical rotations of the configurationally related epimeric heptoses (β-*l*-β-glucoheptose and β-*l*-α-glucoheptose) are known. The epimeric difference (−6,000) obtained from the optical rotations of β-*l*-β-glucoheptose and β-*l*-α-

glucoheptose differs widely from the epimeric difference (+13,200) obtained from the optical rotations of α-*d*-xylose and α-*d*-lyxose. Hence the optical rotations of these substances having the *l*-gulose and *l*-idose configurations do not appear to be in harmony with the optical rotations in the α-*d*-xylose and α-*d*-lyxose series. The epimeric difference (−4,800) obtained from the molecular rotations of β-*l*-altrose and β-*l*-allose may be compared with the epimeric difference for α-*l*-arabinose and α-*l*-ribose. The molecular rotation of α-*l*-arabinose is +28,610. The molecular rotation of α-*l*-ribose is not known, but it can be estimated from the molecular rotation of β-*l*-ribose.[5] By using the calculated value (+12,500) the epimeric difference for α-*l*-arabinose and α-*l*-ribose is found to be+16,110. This value is in accord with the epimeric difference (+14,900) for α-*d*-galactose and α-*d*-talose but differs widely from the value (−4,800) obtained for β-*l*-altrose and β-*l*-allose. The comparisons which have been cited show that the epimeric differences for *d*-xylose and *d*-lyxose resemble those for *d*-glucose and *d*-mannose rather than those for *l*-idose and *l*-gulose, and that the epimeric differences for *l*-arabinose and *l*-ribose resemble those for *d*-galactose and *d*-talose rather than those for *l*-altrose and *l*-allose.

3. COMPARISONS OF THE MOLECULAR ROTATIONS OF SUBSTANCES DIFFERING IN THE CONFIGURATION OF CARBON 3

If the induced dissymmetry at carbon 5 is neglected, *d*-lyxose and *d*-arabinose differ merely in the configuration of carbon 3 and the difference in their molecular rotations is $2R_3$. α-*d*-Lyxose has the same configuration for the glycosidic carbon as β-*d*-arabinose, and β-*d*-lyxose has the same configuration for the glycosidic carbon as α-*d*-arabinose. A comparison of the value of $2R_3$ (table 10) from α-*d*-lyxose and β-*d*-arabinose with the value of $2R_3$ from β-*d*-lyxose and α-*l*-arabinose shows a larger variation (−12,400 and −17,710) than might be anticipated for substances differing merely in the configuration of a single carbon and having like configurations of adjacent carbon atoms. The difference in the values suggests that another factor influences the rotations. If the ring-forming carbons in the pentoses are dissymmetric and if *d*-lyxose resembles *d*-mannose and *d*-arabinose resembles *l*-galactose, the comparison cited involves not only carbon 3 but also carbon 5, which in turn influences the rotation at carbon 1. Thus the difference in the values appears to be in harmony with a dissymmetric structure for the pyranose ring in the pentose series. Seemingly the configuration of carbon 3 plays an important role in this dissymmetry.

[5] According to Hudson's rule of isorotation, the rotation of α-*l*-ribose is equal to the molecular rotation of β-*l*-ribose (+3,050) plus $2A$ (the difference in the molecular rotations of a pair of alpha and beta sugars having similar configurations. Ribose, mannose, lyxose, rhamnose, and talose presumably have similar configurations for carbons 2 and 5. The values of $2A$ obtained from mannose, lyxose, rhamnose, and talose are 8,300, 11,700, 7,900, and 9,900, respectively. By using the average of these figures for $2A$, the molecular rotation of α-*l*-ribose is calculated to be 3,050+9,450=+12,500.

TABLE 10.—*Differences in the molecular rotations for carbon 3*

Rotational difference. $(B+R_3)-(B-R_3)=2R_3$	Sugars. $2R_3$	Methyl glycosides. $2R_3$
β-*d*-Arabinose—α-*d*-lyxose	−12, 400	−12, 500
α-*d*-Arabinose—β-*d*-lyxose	−17, 710	−19, 270
α-*d*-Gulose—α-*d*-galactose	−16, 050	−14, 970
β-*d*-Gulose—β-*d*-galactose		−16, 180

IV. NOMENCLATURE OF THE HIGHER SUGARS AND THEIR DERIVATIVES

Several of the new compounds prepared in the course of this investigation belong to the heptose series. Because of the confusion[6] which exists with respect to the nomenclature of the higher sugars, the several systems of nomenclature in current use will be considered, and our compounds will be named in accordance with each system.

Naming the heptoses and their derivatives involves:

1. Classification in the *d* or *l* configurational series.
2. Classification of the alpha and beta modifications.
3. Selection of specific names.

The terms *d* and *l* frequently have been used to represent both configuration and direction of optical rotation. In the carbohydrate field the *d* and *l* prefixes ordinarily refer to configuration; in other fields they usually relate to the direction of the optical rotation. Some workers prefer to use *D* and *L* to indicate configuration, and to use the small letters to indicate optical rotation, but in this paper the small letters are used to indicate configuration. The substances are classified in the *d* series when the terminal asymmetric carbon has the same configuration as in *d*-glyceric aldehyde [42, 43]; otherwise they are classified in the *l* series.

The alpha and beta prefixes are used to distinguish between the two modifications of a single ring form. Thus the two pyranose modifications of glucose are known as α-*d*-glucose and β-*d*-glucose. The enantiomorph of α-*d*-glucose is called α-*l*-glucose. In other words, the mirror image of the α-*d*-sugar is the α-*l*-sugar. As a consequence of this system the alpha-beta nomenclature does not refer to the absolute configuration. According to the nomenclature originated by Hudson [11] the alpha and beta prefixes are assigned from the relative optical rotations of the alpha and beta isomers. If the substance belongs in the *d*-configurational series, the more dextrorotatory member of the alpha-beta pair is called alpha. If the substance belongs in the *l*-configurational series, the more dextrorotatory member is called beta. According to this system, the name of each isomer depends on its optical rotation and on whether it belongs in the *d* or *l* series. Since in the heptoses and higher sugars the asymmetric carbon which determines the classification in the *d* or *l*-configurational series is not part of the pyranose ring, and has no direct bearing on the configuration of the glycosidic carbon, this alpha-beta nomenclature for the higher sugars does not always group substances of like configuration.

[6] The Divisions of Biological Chemistry, Chemical Education, and Sugar Chemistry and Technology of the American Chemical Society have organized a committee to investigate the nomenclature of the sugars and their derivatives, and to make recommendations for obtaining a more uniform practice.

In order to correlate substances of like configuration for the pyranose ring, Isbell [3] suggested basing the alpha and beta nomenclature on the configuration of the glycosidic carbon in relation to the configuration of the ring-forming carbon. According to this proposal, which is followed in this paper, *substances which have like configurations for the glycosidic and ring-forming carbons are called alpha, and substances which have unlike configurations for the glycosidic and ring-forming carbons are called beta.* This results in the classification of substances having like configurations for the five carbons of the pyranose ring in the same alpha or beta group regardless of the configuration of the groups in the side chain of carbon 5. In case the ring-forming carbon is not asymmetric, as in the pentose series, it is necessary to name the isomers arbitrarily. In this publication the names for the alpha and beta modifications of *d*-xylose, *d*-lyxose, *l*-arabinose, and *l*-ribose correspond to the names for the alpha and beta modifications of the configurationally related hexoses, *d*-glucose, *d*-mannose, *d*-galactose, and *d*-talose, respectively.

The terms *alpha* and *beta* have been used not only to differentiate between the two modifications of a single sugar but also as part of the specific names for the higher sugars. Emil Fischer [44] called the higher sugars heptoses, octoses, and nonoses, according to the number of carbon atoms and distinguished between the two epimeric heptoses obtained from a single hexose by the prefixes α and β. The α and β symbols were given *empirically*, the first isomer to be prepared being called alpha and the next beta. The octoses and higher sugars were named in the same manner by merely increasing the number of alpha and beta terms. For example, the first octose obtained from the first heptose to be prepared from *d*-glucose was called *d*-α-α-gluco-octose [45]. With the preparation of many of the higher sugars, the multiple use of alpha and beta in the same name without structural significance becomes objectionable and it appears to be the consensus of opinion that Fischer's nomenclature should be changed. A comparison of the structures of the heptoses with their names reveals a very interesting coincidence: The six heptoses prepared by Emil Fischer show a correlation between the configuration of the second carbon and the name. In the gluco-, manno-, and galacto-heptoses, designated as alpha, the configuration of the second carbon is like that of the terminal asymmetric carbon; in those designated as beta the configuration is opposite. This correlation is accidental because the configurations were not known when the substances were named. Subsequently the guloheptoses were prepared by LaForge [46] and named according to the order in which they were isolated. It so happened that their configurations did not fit in with the relationship noted for the other heptoses. Later Isbell [1, 22] reinvestigated LaForge's guloheptoses and suggested that their names be changed so as to follow the configurational relationships noted for the heptoses prepared by Fischer. According to Isbell's suggestion, the designation of the heptoses as alpha or beta depends upon whether the configuration of the second carbon is the same as, or different from the configuration of the terminal asymmetric carbon. The suggestion was made as the simplest means for remedying a bad condition. The proposal would not affect the names for the other heptoses, would result in a saving of the labor necessary for memorizing the names and configurations, and would

not materially change the position of the reference in the various indexes through the literature. Extension of the same principle to the octoses and higher sugars would also facilitate remembering their structures, but would call for the revision of several names.

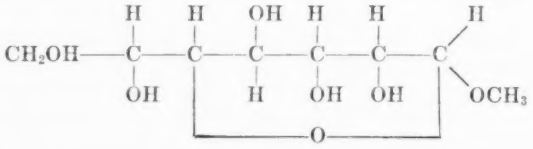
In 1938 Votoček suggested, and has since employed, a system of nomenclature in which he uses the terms *d* and *l* in place of alpha and beta in the specific names of the higher sugars [47, 48]. According to Votoček's proposal, the new methyl *d*-α-galaheptoside which we have prepared would be called α-methyl *d*-gala-*d*-heptopyranoside. The first *d* symbol in the name refers to the configuration of the terminal asymmetric carbon 6; the next *d* symbol refers to the configuration of carbon 2.

In 1938 Hudson also suggested, and has since used, a different system of nomenclature [49, 50, 51]. According to Hudson's system, the name is made up of two parts. The first term depends upon the configurations of carbons 3, 4, 5, and 6, and the second term depends upon the configurations of carbons 2, 3, 4, and 5. For example, the new methyl *d*-α-galaheptoside which we have prepared would be called α-methyl *D*-gala-*L*-mannoheptoside by Hudson. The prefix "*D*-gala" shows that the heptose was derived from *d*-galactose. The second term, "*L*-manno", represents the configurations of carbons 2, 3, 4, and 5 and shows that the substance is configurationally related to *l*-mannose. Each name has two *D* or *L* symbols. The first of these symbols represents the configuration of the terminal asymmetric carbon, and the second represents the configuration of the fifth or pyranose ring-forming carbon. As a basis for naming the alpha and beta isomers, Hudson chooses to use the first *D* or *L* term. If the second *D* or *L* term of his name were to be used as a basis for naming the alpha and beta isomers, the alpha-beta designations which Isbell proposed for the pyranose modifications of the higher sugars would result (see page 140). The methyl *d*-α-galaheptoside designated by Hudson as α-methyl-*D*-gala-*L*-mannoheptoside has the same structure and configuration for the first five carbons as β-methyl *l*-mannoside, and it resembles β-methyl *l*-mannoside very closely. In naming the higher sugars, Hudson takes into consideration the configuration of carbons 2, 3, 4, and 5, but in naming the alpha and beta modifications thereof he abandons the structural and configurational parallelism and bases his names on the terminal asymmetric carbon which lies in the side chain and has no direct bearing on the configuration of the glycosidic carbon. One feature of this system is the overlapping of the groups represented by the prefixes. In this it departs from the established principle of organic chemical nomenclature that such prefixes represent substituent groups. For example, ethylbenzene signifies a benzene molecule with an ethyl group substituted for a hydrogen. Likewise, glucosido-mannose signifies a mannose molecule with a glucosido group substituted for a hydrogen.

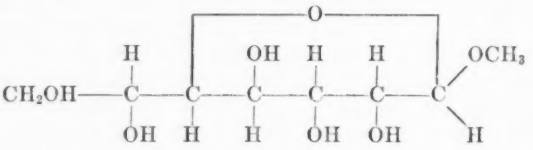
At the meeting of the American Chemical Society in Milwaukee in 1938, C. D. Hurd suggested dropping the first term in Hudson's proposed names and substituting a series of letters to represent the configurations of the higher carbons, beginning with the terminal asymmetric carbon. If the letters *d* and *l* are used to represent the configurations, *d*-α-glucoheptose would be called *d*-*d*-guloheptose. In this name the first symbol represents the configuration of carbon 6, and the second that of carbon 5. The term "*d*-gulo" shows that the sugar

has the *d*-gulose configuration. By naming the alpha and beta isomers according to the configuration of the glycosidic carbon in relation to carbon 5, names result which correlate the alpha and beta modifications of the higher sugars with the alpha and beta modifications of the configurationally related hexoses. As already pointed out, this is advantageous because the reactions and properties of the sugars depend in large measure upon the configurations of the five carbon atoms which comprise the pyranose ring.

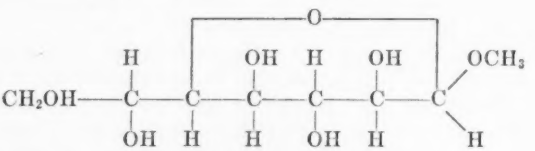
In summary it might be noted that the new heptosides which we have prepared might be represented by the following names:



α-Methyl *d*-*α*-glucoheptopyranoside [7] (Hudson, 1909; Isbell, 1935)
α-Methyl *D*-gluco-*D*-guloheptopyranoside (Hudson, 1938).
α-Methyl *d*-gluco-*d*-heptopyranoside (Votoček, 1938).
α-Methyl *d*-*d*-guloheptopyranoside (Hurd, 1938).



α-Methyl *d*-*α*-galaheptopyranoside (Isbell, 1935).
β-Methyl *d*-*α*-galaheptopyranoside (Hudson, 1909).
β-Methyl *D*-gala-*L*-mannoheptopyranoside (Hudson, 1938).
β-Methyl *d*-gala-*d*-heptopyranoside (Votoček, 1938).
α-Methyl *d*-*l*-mannoheptopyranoside (Hurd, 1938).



α-Methyl *d*-*β*-galaheptopyranoside (Isbell, 1935).
β-Methyl *d*-*β*-galaheptopyranoside (Hudson, 1909).
β-Methyl *D*-gala-*L*-glucoheptopyranoside (Hudson, 1938).
β-Methyl *d*-gala-*l*-heptopyranoside (Votoček, 1938).
α-Methyl *d*-*l*-glucoheptopyranoside (Hurd, 1938).

V. EXPERIMENTAL DETAILS

1. PREPARATION METHODS

(a) PREPARATION OF *α*-METHYL *d*-LYXOPYRANOSIDE

Fifty grams of *d*-lyxose was refluxed for 4 hours with 700 ml of absolute methyl alcohol containing 1.5 percent of hydrogen chloride. A Fehling's test at this time showed the absence of reducing sugar. The solution was cooled and neutralized with silver carbonate. A small quantity of decolorizing carbon was added and after filtration

[7] The term "-pyranoside" was originated by W .N. Haworth.

the solution was concentrated in vacuo to a sirup of about 75 percent total solids. The sirup was warmed with 75 ml of isopropyl alcohol and allowed to stand overnight in the refrigerator. The α-methyl *d*-lyxopyranoside which crystallized was collected on a filter and washed with isopropyl alcohol. The yield was 28 g and a second crop of 8 g separated from the mother liquor. Recrystallization was accomplished by dissolving the crude product in water and concentrating the solution to a sirup (75 percent total solids). After the addition of a threefold quantity of isopropyl alcohol, the mixture was seeded with crystalline α-methyl *d*-lyxopyranoside and allowed to stand. After several hours the crystals were collected on a filter and washed with isopropyl alcohol. The melting point, 108° C, and the specific rotation, $[\alpha]_D^{20} = +59.4$ (water; *c*, 4), agree with the constants reported by Phelps and Hudson [24].

(b) PREPARATION OF β-METHYL *d*-LYXOPYRANOSIDE

The mother liquor from the preparation of α-methyl *d*-lyxopyranoside was concentrated and allowed to stand in a desiccator for several weeks, whereupon crystallization occurred spontaneously. The crystals (5.5 g) were separated and found to be a mixture of the alpha and beta isomers with a specific rotation of −15°. The mixture was recrystallized by dissolving it in a minimum quantity of hot isopropyl alcohol (about sixfold), treating with activated carbon, filtering, and cooling. Fractional recrystallization yielded about 1 g of pure crystalline β-methyl *d*-lyxopyranoside and a crystalline mixture of the isomers which has not been separated. β-Methyl *d*-lyxopyranoside crystallizes in slender prisms (fig. 1,*A*), which melt at 118° C, and give $[\alpha]_D^{20} = -128.1$ (water; *c*, 2.5). When pure, the substance crystallizes readily from water, as well as from isopropyl alcohol. *Analysis:* Calculated for $C_5H_{12}O_5$: C, 43.90; H, 7.37. Found: C, 44.19; H, 7.25. The new substance was shown to be a pyranoside by periodic oxidation. A sample (0.164 g) was dissolved in 11 ml of 0.2 *M* periodic acid and the solution held at 20° C. The optical rotation was read and after about 1 hour became nearly constant at −8.67° S in a 2-dm tube. The observed rotation reduced to the basis of the dialdehyde corresponds to $[\alpha]_D^{20} = -125.5°$. This value is approximately equal in magnitude but is of opposite sign to that found by Maclay and Hudson [7] for the product from α-methyl *d*-lyxopyranoside. The residual periodic acid was determined by titration with sodium arsenite. The titration showed that periodic acid had been used in the ratio of 2.06 moles per mole of β-methyl *d*-lyxopyranoside.

(c) PREPARATION OF β-METHYL TRIACETYL-*d*-LYXOPYRANOSIDE

Four-tenths gram of pure crystalline β-methyl *d*-lyxopyranoside was warmed slightly with 5 ml of acetic anhydride and 0.5 g of fused and powdered sodium acetate. The reaction mixture, after standing overnight, was poured into cracked ice, extracted with chloroform, and the chloroform removed by evaporation in vacuo. After the addition of a little water, the new substance crystallized. The crude acetate (0.66 g) was recrystallized from water, in which it is difficultly soluble. β-Methyl triacetyl-*d*-lyxopyranoside crystallizes in large truncated prisms (fig. 1,*B*), which melt at 88 to 89° C, and give $[\alpha]_D^{20} = -109.5$ (chloroform; *c*, 4.5). *Analysis:* Calculated for $C_{12}H_{18}O_8$: C, 49.65; H, 6.25. Found: C, 50.10; H, 6.49.

(d) PREPARATION OF β-METHYL TETRA-ACETYL-*d*-MANNOPYRANOSIDE

β-Methyl tetra-acetyl-*d*-mannopyranoside was prepared in small quantity from triacetyl *d*-mannose 1,2-methyl orthoacetic ester by the method originally used by Dale [39]. Since the yield by this method was extremely small, the dimethyl sulfate method previously used by Schlubach [52] for the preparation of β-methyl *d*-glucopyranoside was adopted. The preparation was conducted in the following manner: 18 g of *d*-mannose was dissolved in 100 ml of water at 0° C; dimethyl sulfate was added dropwise to the cold solution over a period of about 3 hours while the mixture was maintained alkaline to acyl blue (pH 12) by the dropwise addition of a 30-percent solution of sodium hydroxide. A total of 20 to 22 ml of alkali was added in the course of 8 hours. After standing overnight at room temperature, the solution was neutralized, treated with activated carbon, filtered, and concentrated in vacuo to a volume of approximately 30 ml. The sirup was mixed with 60 ml of dioxane and the evaporation was repeated to facilitate dehydration. The resulting thick sirup was dissolved in 60 ml of pyridine and acetylated by the addition of 60 ml of acetic anhydride. After standing overnight at room temperature, the solution was poured into cracked ice and the gummy precipitate extracted with chloroform. The extract was washed successively with solutions of sodium bicarbonate, copper sulfate (until free from pyridine) and water. The chloroform solution was dried, treated with decolorizing carbon, filtered and evaporated to a thin sirup. One hundred milliliters of ethyl alcohol was added and the solution concentrated to a sirup which crystallized spontaneously. The material was removed from the flask with 100 ml of ether. Petroleum ether was then added to saturation. After the solution had stood for a day at 0° C, the crystals were collected on a filter and washed with a mixture of ether and petroleum ether. The yield of the mixed α- and β-methyl tetra-acetyl-*d*-mannopyranoside was about 18 g. The crude product was stirred with 100 ml of ether and filtered. The residue, about 6 g, was fairly pure β-methyl tetra-acetyl-*d*-mannopyranoside. The compound after recrystallization from 1.5 parts of 95-percent ethyl alcohol was substantially pure and gave a melting point of 159° to 160° C, and a specific rotation of −47.8°, in agreement with the constants reported by Dale [39]. Several prior investigators have deacetylated β-methyl tetra-acetyl-*d*-mannopyranoside to give β-methyl-*d*-mannopyranoside in the form of a sirup [53, 54]. In the early stages of the present investigation, a crystalline calcium chloride compound of β-methyl *d*-mannopyranoside was separated, and it was planned to use this compound for the purification of the glycoside in the manner which one of us has found useful for purifying the α- and β-methyl *d*-gulopyranosides, but before this plan was completed a crystalline methyl mannopyranoside containing isopropyl alcohol of crystallization was obtained.

(e) PREPARATION OF β-METHYL *d*-MANNOPYRANOSIDE ISOPROPYL ALCOHOLATE

Twenty-five grams of β-methyl tetra-acetyl-*d*-mannopyranoside was deacetylated with a small quantity of barium methylate [5], using 500 ml of absolute methyl alcohol and 10 ml of water-free barium methylate solution (about 0.6 *N*). After the barium methylate had been decomposed by an equivalent quantity of sulfuric acid and the barium sulfate separated by filtration, the filtrate was evaporated in

vacuo to a thin sirup (about 15 ml). Forty milliliters of isopropyl alcohol was added and the methyl mannoside containing isopropyl alcohol of crystallization ($C_7H_{14}O_6.C_3H_8O$) separated in large thin plates (fig. 1, *D*). The yield was almost quantitative. To recrystallize, the substance was dissolved in 15 parts of boiling isopropyl alcohol and allowed to stand overnight at 0° C. The crystals were collected on a filter, washed with cold isopropyl alcohol, and dried for 24 hours over calcium chloride. β-Methyl *d*-mannopyranoside isopropyl alcoholate melts at 74° to 75° C and gives $[\alpha]_D^{20} = -53.3$ (water; *c*, 4). This value is equivalent to a specific rotation of −69.8 for β-methyl *d*-mannopyranoside. The crystals have a slight odor of isopropyl alcohol and decompose on standing in an open container. They are stable in the presence of isopropyl alcohol vapor. A sample heated at 105° C in vacuo came to constant weight in 12 hours. Loss calculated for 1 molecule of isopropyl alcohol: 23.45 percent. Found: 23.21 percent. The colorless glassy residue would not crystallize from other solvents, but crystallized readily upon addition of more isopropyl alcohol. A sample of β-methyl *d*-mannopyranoside isopropyl alcoholate was placed in a combustion tube and heated at 77° C in a current of dry oxygen. Under the conditions of the experiment, 70.0 percent of the isopropyl alcohol was volatilized and analyzed. Calculated for C_3H_8O: C, 59.96; H, 13.42. Found: C, 58.56; H, 12.78. The residue was analyzed separately. Calculated for 30.0 percent β-methyl *d*-mannopyranoside isopropyl alcoholate and 70 percent β-methyl *d*-mannopyranoside: C, 44.35; H, 7.68. Found: C, 44.77; H, 8.17.

(f) PREPARATION OF α-METHYL *d*-GALAHEPTOPYRANOSIDE

The methyl heptoside which has the α-methyl *d*-mannopyranoside structure was prepared first by Hann, Merrill, and Hudson [29]. They called the substance β-methyl *d*-α-galaheptopyranoside. In accordance with nomenclature used in this article, we shall designate it as α-methyl *d*-α-galaheptopyranoside. We repeated the preparation of this compound and found its properties to be in substantial agreement with those reported by Hann, Merrill, and Hudson.

(g) PREPARATION OF β-METHYL PENTA-ACETYL-*d*-α-GALAHEPTOPYRANOSIDE

The methyl heptoside having the β-methyl *d*-mannopyranoside configuration (β-methyl *d*-α-galaheptopyranoside) resembles β-methyl *d*-mannopyranoside in that it does not crystallize under the conditions which usually give crystalline products. Using the dimethyl sulfate method followed by acetylation, as in the case of mannose, we obtained the glycoside in the form of a crystalline acetate.

d-α-Galaheptose hydrate (22.8 g) was methylated with dimethyl sulfate in alkaline solution and acetylated as described for the preparation of β-methyl tetra-acetyl-*d*-mannopyranoside. The chloroform solution containing the acetylated product was evaporated in vacuo to a thin sirup, which was taken up in ethyl alcohol. The alcoholic mixture was then evaporated again and the resulting sirup taken up in 40 ml of ether. The ether solution was saturated with petroleum ether and was allowed to stand overnight at 0° C. The crystals which formed were collected on a filter and washed with a mixture of absolute alcohol and petroleum ether. The yield was 4.1 g. A second crop of 2.5 g was obtained from the mother liquor. The

compound was recrystallized from 4 or 5 parts of boiling 95-percent ethyl alcohol. β-Methyl penta-acetyl-*d*-α-galaheptopyranoside separates in slender prisms (fig. 1, *E*) which melt at 171° to 173° C and give $[\alpha]_D^{20}=+77.6$ (chloroform; *c*, 4). *Analysis:* Calculated for $C_{18}H_{26}O_{12}$: C, 49.77; H, 6.03. Found: C, 49.67; H, 5.94.

(h) PREPARATION OF β-METHYL *d*-α-GALAHEPTOPYRANOSIDE

Five and one-half grams of pure β-methyl penta-acetyl-*d*-α-galaheptopyranoside was suspended in 110 ml of absolute methyl alcohol, cooled to 0° C, and deacetylated by treatment with 5 ml of water-free barium methylate solution, as in the preparation of β-methyl tetra-acetyl mannopyranoside. After removal of the barium, and concentration, a sirup was obtained which could not be brought to crystallization. The rate of hydrolysis and the optical properties of the amorphous product, however, were studied. The dry weight was determined on an aliquot part of the sirup by heating it in vacuo at 105° C after a preliminary evaporation of the solvent at a lower temperature (60° C). The sirup lost weight rapidly during 1 hour at 105° C. and afterwards there was a small gradual loss, apparently due to volatilization of the glycoside. Based upon the weight of the substance dried for 1 hour at 105° C, $[\alpha]_D^{20}=+74$.

(i) PREPARATION OF β-METHYL *d*-α-GLUCOHEPTOPYRANOSIDE

β-Methyl *d*-α-glucoheptopyranoside was prepared by the method of Fischer [28]. Forty grams of *d*-α-glucoheptose was refluxed for 6 hours with 400 ml of absolute methyl alcohol containing 1.5 percent of hydrogen chloride. After neutralization with silver carbonate, the solution was treated with activated carbon, filtered, and evaporated to a sirup of about 85 percent total solids. This was dissolved in 25 ml of ethyl alcohol, and after the addition of 25 ml of isopropyl alcohol, the solution was allowed to stand overnight at 0° C. The crystals of β-methyl *d*-α-glucoheptopyranoside which formed were collected on a filter and washed with a mixture of ethyl alcohol and isopropyl alcohol (1:1). The yield was 23.5 g. The crude product was recrystallized from a sixteenfold quantity of boiling 95-percent ethyl alcohol. The substance melted at 170° C and gave $[\alpha]_D^{20}=-74.7$, in substantial agreement with the properties reported by Fischer.

(j) PREPARATION OF α-METHYL *d*-α-GLUCOHEPTOPYRANOSIDE.$CaCl_2.H_2O$

The usual methods for the preparation of crystalline methyl glycosides have not been successful for the preparation of crystalline α-methyl *d*-α-glucoheptopyranoside. However, we anticipated that the procedure which had proved successful for the preparation of the configurationally related guloside [4] would be suitable for obtaining this heptoside. This proved to be the case and a crystalline calcium chloride compound of α-methyl *d*-α-glucoheptopyranoside was separated, from which crystalline α-methyl *d*-α-glucoheptopyranoside was obtained after removal of the calcium chloride with silver sulfate.

The mother liquor from the preparation of β-methyl *d*-α-glucoheptopyranoside just described was concentrated to a sirup of about 85 percent total solids. The amount of calcium chloride molecularly equivalent to the glycoside in the mother liquor was calculated from the difference between the theoretical amount of glycoside formed on

methylation and the weight of the crystalline β-methyl glycoside removed. In the preparation reported, 12.6 g of $CaCl_2.2H_2O$ was added to the mother liquor of the β-methyl *d*-α-glucoheptopyranoside. The mixture was concentrated to a thick sirup, which crystallized spontaneously. The crystals of the calcium chloride compound of α-methyl *d*-α-glucoheptopyranoside were collected on a filter and washed with 95 percent ethyl alcohol. The yield was 12.5 g. To recrystallize, the compound was dissolved in water and concentrated in vacuo to a sirup of about 75 percent total solids. A small amount of alcohol was added and the sirup was seeded and rotated during crystallization. The crystals were separated and washed with alcohol. The calcium chloride compound of α-methyl *d*-α-glucoheptopyranoside crystallizes in large colorless hexagonal plates (fig. 1, *F*) and gives $[\alpha]_D^{20} = +69.1$ (water; *c*, 4). *Analysis:* Calculated for $C_8H_{16}O_7.CaCl_2.H_2O$: C, 27.20; H, 5.14; Ca, 11.45; Cl, 19.90. Found: C, 27.17; H, 5.14; Ca, 11.35; Cl, 20.08.

(k) PREPARATION OF α-METHYL *d*-α-GLUCOHEPTOPYRANOSIDE

Ten grams of pure α-methyl *d*-α-glucoheptopyranoside.$CaCl_2.H_2O$ was dissolved in 25 ml of water and the solution shaken with an excess of silver sulfate until a test for chloride was negative. After the addition of decolorizing carbon, the mixture was filtered and the filtrate evaporated in vacuo to a heavy sirup, which was then taken up in a small amount of isopropyl alcohol and allowed to stand in a desiccator. α-Methyl *d*-α-glucoheptopyranoside crystallized in nearly quantitative yield. The crude glycoside was dissolved in a minimum quantity of boiling absolute ethyl alcohol and the sirup diluted with one-third its volume of isopropyl alcohol. The solution was cooled and allowed to stand in a desiccator overnight. The crystals were separated on a filter and washed several times with a mixture of 9 parts of absolute alcohol and 1 part of isopropyl alcohol. By the crystallization of additional crops from the mother liquor, practically all of the glycoside was recovered. α-Methyl *d*-α-glucoheptopyranoside crystallizes in rectangular prisms, many of them truncated (fig. 1, *H*). It melts at 106° to 107° C and gives $[\alpha]_D^{20} = +111.5$ (water; c, 4). *Analysis:* Calculated for $C_8H_{16}O_7$: C, 42.85; H, 7.19. Found: C, 42.75; H, 7.12.

(l) PREPARATION OF α-METHYL PENTA-ACETYL-*d*-α-GLUCOHEPTOPYRANOSIDE

One-half gram of α-methyl *d*-α-glucoheptopyranoside was treated with 5 ml of acetic anhydride and 0.5 g of freshly fused and powdered sodium acetate. The reaction mixture was warmed slightly and then allowed to stand at room temperature for several hours, after which it was poured into ice water. α-Methyl penta-acetyl-*d*-α-glucoheptopyranoside crystallized from the water mixture. The crystals (fig. 1, *I*) were collected on a filter and dried in vacuo. The compound was recrystallized from 25 ml of boiling 95 percent ethyl alcohol. It melts at 174° to 175° C and gives $[\alpha]_D^{20} = +107.4$ (chloroform; *c*, 4). *Analysis:* Calculated for $C_{18}H_{26}O_{12}$: C, 49.77; H, 6.03. Found: C, 49.67; H, 5.94. Our compound appears to differ from the product of Haworth, Hirst, and Stacey [12], which is reported to melt at 169° C and to give $[\alpha]_D^{20} = +91°$. Further investigation is necessary to show wherein the two products differ.

(m) PREPARATION OF (β-METHYL *d*-α-GLUCOHEPTOPYRANOSIDE)$_2$.$CaCl_2.2H_2O$

Pure β-methyl *d*-α-glucoheptopyranoside (7.7 g) was mixed with an equimolecular quantity of calcium chloride (5.1 g of $CaCl_2.2H_2O$) and the mixture dissolved in 15 ml of water. The solution was filtered, diluted with 2 volumes of ethyl alcohol, and allowed to stand for several days in a desiccator. The slender prismatic crystals (fig. 1, *G*) which formed almost quantitatively were separated on a filter and washed with 95-percent ethyl alcohol. The compound was recrystallized from a large volume of boiling 95-percent ethyl alcohol and dried for 24 hours over calcium chloride in a vacuum desiccator. *Analysis:* Calculated for $(C_8H_{16}O_7)_2.CaCl_2.2H_2O$: C, 32.27; H, 6.09; Ca, 6.73; Cl, 11.91. Found: C, 32.27; H, 6.00; Ca, 6.67; Cl, 11.88. The new product gave $[\alpha]_D^{20}=-56.1$ (water; *c*, 4).

(n) PREPARATION OF α-METHYL *d*-LYXOPYRANOSIDE.$CaCl_2.2H_2O$

Pure α-methyl *d*-lyxopyranoside (3.3 g) was dissolved with an equivalent quantity of calcium chloride (3 g of $CaCl_2.2H_2O$) in 5 ml of water. The solution was filtered and evaporated in a desiccator to a thick sirup, which was taken up in a few drops of isoamyl alcohol. After this had stood for several days in a desiccator, α-methyl *d*-lyxopyranoside-calcium chloride crystallized in slender rectangular plates (fig. 1, *C*), which were separated and washed with isoamyl alcohol. The product was recrystallized by dissolving it in water, evaporating the solution in a desiccator, and adding isoamyl alcohol. The recrystallized product was slightly hygroscopic, but stable in dry air. For analysis, it was dried at room temperature for several days over calcium chloride. It gives $[\alpha]_D^{20}=+31.3$ (water; *c*, 2). *Analysis:* Calculated for $C_6H_{12}O_5.CaCl_2.2H_2O$: Ca, 12.88; Cl, 22.79. Found: Ca, 12.87; Cl, 22.75.

(o) PREPARATION OF α-METHYL *d*-β-GALAHEPTOPYRANOSIDE

Five grams of *d*-β-galaheptose was refluxed for 6 hours with 100 ml of methyl alcohol containing 1.5 g of hydrogen chloride. The solution was cooled and neutralized with silver carbonate. The resulting silver chloride was separated, and the solution was evaporated under reduced pressure to a heavy sirup, which crystallized spontaneously. The semisolid crystalline mass was mixed with 30 ml of isopropyl alcohol. After the mixture had stood for several hours, the crystals were separated by filtration and washed with isopropyl alcohol. The crystalline product weighed 45 g, melted at 150° C, and gave $[\alpha]_D^{20}=-86$ (water; *c*, 4). It proved to be a mixture containing a more highly levorotatory product. Upon recrystallization from a mixture of ethyl and isopropyl alcohols, the more difficultly soluble fractions gave a specific rotation of -48 to -80, while the crystals obtained from the mother liquors gave specific rotations from -80 to -107.8. The optical rotation of the product, $[\alpha]_D^{20}=-108$ (water; *c*, 4), did not change on further recrystallization, and hence it is believed that it is a pure compound. The clusters of needle-like crystals (fig. 1, *J*) melt at 154° to 155° C and give the following analysis: Calculated for $C_8H_{16}O_7$: C, 42.85; H, 7.19. Found: C, 42.97; H, 7.34.

Our product, which resembles α-methyl *l*-glucopyranoside is the second methyl glycoside of *d*-β-galaheptose to be prepared. The heretofore known methyl *d*-β-galaheptopyranoside prepared by Hann

FIGURE 1.—*Photomicrographs of new glycosides.*

A—β-Methyl d-lyxopyranoside.
B—β-Methyl triacetyl-d-lyxopyranoside.
C—α-Methyl d-lyxopyranoside.$CaCl_2.2H_2O$.
D—β-Methyl d-mannopyranoside isopropyl alcoholate.
E—β-Methyl penta-acetyl d-α-galaheptopyranoside.

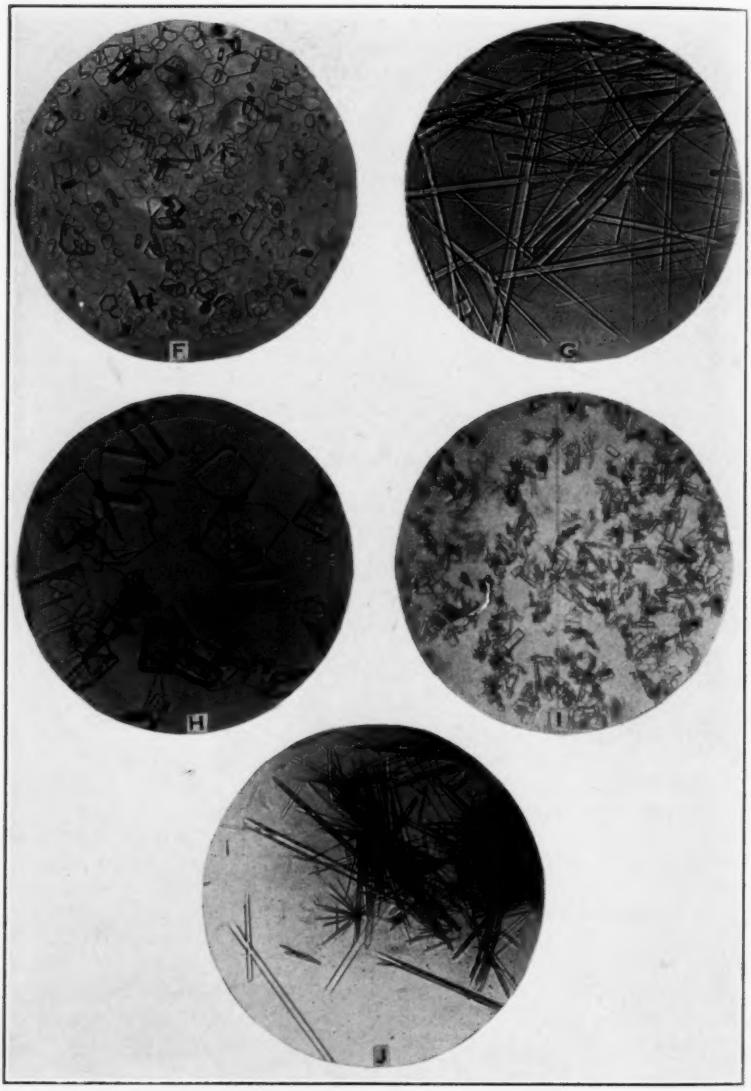


FIGURE 1 (Continued).—*Photomicrographs of new glycosides.*

F—α-Methyl d-α-glucoheptopyranoside.$CaCl_2.H_2O$.
G—(β-Methyl d-α-glucoheptopyranoside)$_2.CaCl_2.2H_2O$.
H—α-Methyl d-α-glucoheptopyranoside.
I—α-Methyl penta-acetyl d-α-glucoheptopyranoside.
J—α-Methyl d-β-galaheptopyranoside.

and Hudson [30] gives a specific rotation of +36 and is closely related to β-methyl *l*-glucopyranoside. Since the glycosidic and ring-forming carbons have like configurations in our product, we have named it α-methyl *d*-β-galaheptopyranoside. According to Hudson's alpha-beta nomenclature, it would be named β-methyl *d*-β-galaheptopyranoside.

2. MEASUREMENT OF RATES OF HYDROLYSIS

The measurements at 98° C were conducted in the following manner: The crystalline glycoside (usually 0.4 g) was dissolved in 10 ml of 0.05 *N* HCl. The optical rotation was read at 20° C, and then the polariscope tube containing the solution was immersed in a bath of boiling water. Time was measured beginning with the immersion of the tube. The polariscope tube was closed by a stopper carrying a thermometer which dipped into the solution. After a suitable time interval, the tube was removed from the bath and plunged into a mixture of ice and water. After 45 seconds the temperature dropped to approximately 20° C, and the tube was then removed from the ice bath and the optical rotation read at 20° C. The tube was then inserted in the boiling water bath and heated again. The process was repeated a number of times, thereby furnishing check values for the velocity constant. It required about 5 minutes to cool the tube and make the polariscope readings. Since the reaction at 20° C is slow in comparison with the reaction at 98° C, the time that the sample was held at the lower temperature was not included in calculating the velocity constants. The velocity constants were calculated from the usual equation:

$$k=\frac{1}{t}\log\frac{r_0-r_\infty}{r_t-r_\infty},$$

where r_0 is the rotation of the solution at the beginning of the hydrolysis, r_∞ the rotation when hydrolysis is complete, and r_t the rotation at the time, t. Inasmuch as some of the hydrolyses were very slow, the value of r_∞ was calculated from the specific rotations of the methyl glycosides and the sugar formed by hydrolysis.

The measurements at 75° C were conducted in the following manner: A freshly prepared solution of the glycoside in 0.5 *N* HCl at 75° C was placed in a water-jacketed polariscope tube, which was maintained at the desired temperature by circulating water. From time to time, the optical rotations were read and recorded. The velocity constants, as given in table 2, were calculated from the usual equation.

VI. SUMMARY

Velocity constants are given for the hydrolysis of the α- and β-methyl *d*-lyxopyranosides, *d*-mannopyranosides, *d*-gulopyranosides, *d*-α-galaheptopyranosides, *d*-β-galaheptopyranosides, and *d*-α-glucoheptopyranosides. The configurations of all of the carbons comprising the pyranose ring affect the rate of hydrolysis. Aldopyranosides having *trans* configurations for carbons 1 and 3 are hydrolyzed more slowly than the corresponding modifications having *cis* configurations for carbons 1 and 3. The molecular rotations of the methyl glycopyranosides are compared according to the configurations of carbons 1, 2, and 3, and certain relationships have been found to support the classification of the methyl lyxopyranosides in the *d*-mannose series rather than in the *l*-gulose series.

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The preparation and properties of the following new compounds given:

β-Methyl d-lyxopyranoside and β-methyl triacetyl-d-lyxopyranoside.—The mother liquor of α-methyl *d*-lyxopyranoside prepared by Fischer's hydrogen chloride method yields a small amount of crystalline β-methyl *d*-lyxopyranoside, mp 118°C, $[\alpha]_D^{20}=-128.1$ (water; *c*, 2.5). Acetylation of β-methyl *d*-lyxopyranoside with acetic anhydride and sodium acetate yields crystalline β-methyl triacetyl-*d*-lyxopyranoside, mp 88° to 89°C, $[\alpha]_D^{20}=-109.5$ (chloroform; *c*, 4.5). Addition of calcium chloride to α-methyl *d*-lyxopyranoside gives α-methyl *d*-lyxopyranoside.$CaCl_2.2H_2O$, $[\alpha]_D^{20}=+31.3$ (water; *c*, 2).

β-Methyl d-mannopyranoside isopropyl alcoholate.—Treatment of *d*-mannose with 1 equivalent of dimethyl sulfate and alkali, followed by the acetylation of the product, gives β-methyl tetra-acetyl *d*-mannopyranoside (6 g from 18 g of mannose). Deacetylation with barium methylate in methyl alcoholic solution and subsequent evaporation of the methyl alcohol and addition of isopropyl alcohol gives crystalline β-methyl *d*-mannopyranoside isopropyl alcoholate. This compound loses isopropyl alcohol readily, mp 74° to 75°C, $[\alpha]_D^{20}=-53.3$ (water; *c*, 4).

β-Methyl d-α-galaheptopyranoside and β-methyl penta-acetyl-d-α-galaheptopyranoside.—Treatment of *d*-α-galaheptose with 1 equivalent of dimethyl sulfate and alkali, followed by acetylation of the product, gives a new crystalline methyl penta-acetyl-*d*-α-galaheptopyranoside, mp 171° to 173°C, $[\alpha]_D^{20}=+77.6$ (chloroform; *c*, 4). Deacetylation with barium methylate in methyl alcoholic solution gives a new methyl *d*-α-galaheptopyranoside which could not be brought to crystallization, $[\alpha]_D^{20}=+74$.

α-Methyl d-α-glucoheptopyranoside.$CaCl_2.H_2O$ *and* (*β-methyl d-α-glucoheptopyranoside*)$_2$.$CaCl_2.2H_2O$.—Treatment of *d*-α-glucoheptose with methyl alcohol containing 1.5 percent of hydrogen chloride gives β-methyl *d*-α-glucoheptopyranoside in 55-percent yield; the mother liquor by treatment with calcium chloride yields crystalline α-methyl *d*-α-glucoheptopyranoside.$CaCl_2.H_2O$, $[\alpha]_D^{20}=+69.1$ (water; *c*, 4). Crystalline (β-methyl *d*-α-glucoheptopyranoside)$_2$.$CaCl_2.2H_2O$ prepared from the glycoside and calcium chloride gives $[\alpha]_D^{20}=-56.1$ (water; *c*, 4).

α-Methyl d-α-glucoheptopyranoside and α-methyl penta-acetyl-d-α-glucoheptopyranoside.—Removal of the calcium chloride from α-methyl *d*-α-glucoheptopyranoside.$CaCl_2.H_2O$ with silver sulfate gives crystalline α-methyl *d*-α-glucoheptopyranoside, mp 106° to 107° C, $[\alpha]_D^{20}=+111.5$ (water; *c*, 4). Acetylation with acetic anhydride and sodium acetate yields crystalline α-methyl penta-acetyl-*d*-α-glucoheptopyranoside, mp 174° to 175° C, $[\alpha]_D^{20}=+107.4$ (chloroform; *c*, 4). This acetate differs from the product described by Haworth, Hirst, and Stacey.

α-Methyl d-β-galaheptopyranoside.—Treatment of *d*-β-galaheptose with methyl alcohol containing hydrogen chloride gives crystalline methyl *d*-β-galaheptopyranoside, mp 154° to 155° C, $[\alpha]_D^{20}=-108$ (water; *c*, 4) in addition to a mixed product, $[\alpha]_D^{20}=-48$.

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VII. REFERENCES

[1] H. S. Isbell, J. Research NBS **18,** 505 (1937) RP990.
[2] H. S. Isbell and W. W. Pigman, J. Research NBS **18,** 141 (1937) RP969.
[3] H. S. Isbell, J. Chem. Education **12,** 96 (1935).
[4] H. S. Isbell, BS J. Research **8,** 1 (1932) RP396.
[5] H. S. Isbell, BS J. Research **5,** 1185 (1930) RP253.
[6] E. L. Jackson and C. S. Hudson, J. Am. Chem. Soc. **59,** 994 (1937).
[7] W. P. Maclay and C. S. Hudson, J. Am. Chem. Soc. **60,** 2059 (1938).
[8] E. F. Armstrong, Proc. Roy. Soc. (London) **74,** 192 (1904).
[9] C. N. Riiber and N. A. Sørensen, Det. Kgl. Norske Videnskab Selskabs Skrifter, no. 1, p. 1 (1938).
[10] W. N. Haworth and E. L. Hirst, J. Chem. Soc. **1930,** 2615.
[11] C. S. Hudson, J. Am. Chem. Soc. **31,** 66 (1909).
[12] W. N. Haworth, E. L. Hirst, and M. Stacey, J. Chem. Soc. **1931,** 2864.
[13] W. N. Haworth, The Constitution of Sugars, p. 91 (Edward Arnold & Co., London, 1929).
[14] E. Pacsu, J. Am. Chem. Soc. **61,** 2669 (1939).
[15] C. S. Hudson, J. Am. Chem. Soc. **61,** 2972 (1939).
[16] C. S. Hudson and E. Yanovsky, J. Am. Chem. Soc. **39,** 1013 (1917).
[17] W. W. Pigman and H. S. Isbell, J. Research NBS **19,** 189 (1937) RP1021.
[18] W. C. Austin and F. L. Humoller, J. Am. Chem. Soc. **55,** 2167 (1933); **56,** 1153 (1934).
[19] H. S. Isbell, BS J. Research **5,** 741 (1930) RP226.
[20] H. S. Isbell, J. Am. Chem. Soc. **56,** 2789 (1934).
[21] H. S. Isbell, J. Research NBS **20,** 97 (1938) RP1069.
[22] H. S. Isbell, J. Research NBS **19,** 639 (1937) RP1052.
[23] C. S. Hudson, J. Am. Chem. Soc. **47,** 265 (1925).
[24] F. P. Phelps and C. S. Hudson, J. Am. Chem. Soc. **48,** 503 (1926).
[25] C. N. Riiber, Ber. deut. chem. Ges. **57,** 1797 (1924).
[26] E. Fischer and L. Beensch, Ber. deut. chem. Ges. **29,** 2927 (1896).
[27] C. N. Riiber, J. Minsaas, and R. T. Lyche, J. Chem. Soc. **1929,** 2173.
[28] E. Fischer, Ber. deut. chem. Ges. **28,** 1145 (1895).
[29] R. M. Hann, A. T. Merrill, and C. S. Hudson, J. Am. Chem. Soc. **57,** 2100 (1935).
[30] R. M. Hann and C. S. Hudson, J. Am. Chem. Soc. **59,** 548 (1937).
[31] C. S. Hudson and J. K. Dale, J. Am. Chem. Soc. **40,** 997 (1918).
[32] J. K. Dale, J. Am. Chem. Soc. **37,** 2745 (1915).
[33] F. P. Phelps and C. S. Hudson, J. Am. Chem. Soc. **50,** 2049 (1928).
[34] C. S. Hudson and J. K. Dale, J. Am. Chem. Soc. **37,** 1264 (1915).
[35] T. L. Harris, E. L. Hirst, and C. E. Wood, J. Chem. Soc. **1932,** 2108.
[36] F. Micheel and O. Littmann, Liebigs Ann. Chem. **466,** 115 (1928).
[37] J. K. Dale and C. S. Hudson, J. Am. Chem. Soc. **52,** 2534 (1930).
[38] W. N. Haworth and E. L. Hirst, J. Chem. Soc. **1928,** 1221.
[39] J. K. Dale, J. Am. Chem. Soc. **46,** 1046 (1924).
[40] C. S. Hudson, J. Am. Chem. Soc. **48,** 1434 (1926).
[41] K. Freudenberg and R. Kuhn, Ber. deut. chem. Ges. **64,** 703 (1931).
[42] M. Rosanoff, J. Am. Chem. Soc. **28,** 525 (1906).
[43] A. Wohl and K. Freudenberg, Ber. deut. chem. Ges. **56,** 309 (1923); **58,** 451 (1925).
[44] E. Fischer, Ber. deut. chem. Ges. **23,** 934 (1890).
[45] E. Fischer, Liebigs Ann. Chem. **270,** 92 (1892).
[46] F. B. LaForge, J. Biol. Chem. **41,** 251 (1920).
[47] E. Votoček, Collection Czechoslov. Chem. Communications **10,** 264 (1938).
[48] E. Votoček, Collection Czechoslov. Chem. Communications **10,** 273 (1938).
[49] C. S. Hudson, J. Am. Chem. Soc. **60,** 1537 (1938).
[50] R. M. Hann, W. D. Maclay, A. E. Knauf, and C. S. Hudson, J. Am. Chem. Soc. **61,** 1268 (1939).
[51] R. M. Hann, W. D. Maclay, and C. S. Hudson, J. Am. Chem. Soc. **61,** 1270 (1939).
[52] H. H. Schlubach and K. Maurer, Ber. deut. chem. Ges. **57,** 1686 (1924).
[53] E. L. Jackson and C. S. Hudson, J. Am. Chem. Soc. **61,** 959 (1939).
[54] F. Klages and R. Maurenbrecher, Liebigs Ann. Chem. **535,** 182 (1938).

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FIRST SPECTRUM OF TIN

By William F. Meggers

ABSTRACT

The spectrum emitted by neutral tin atoms has been measured, compiled, and analyzed. Revised wavelengths and relative intensities are given for 378 lines, 341 of which were observed photographically (1697.59 to 12536.5 A), and 37 of greater wavelengths (12788.2 to 24738.2 A) were measured radiometrically by Randall and Wright. About 80 percent of these lines are classified as combinations of energy levels arising from $5p^2$, $5pns$, $5pnp$, $5pnd$, and $5pnf$ electron configurations. The average difference between observed and computed wave numbers for lines measured photographically is 0.09 cm^{-1}. Four series of the type $5p^2-5pns$ yield a mean absolute value of 59155 cm^{-1} for the ground level, $5p^2\ ^3P_0$, of neutral tin atoms. From this, the principal ionization potential of tin is calculated to be 7.297 volts.

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I. INTRODUCTION

Several years ago, when the Research Laboratory of the Eastman Kodak Co. first produced the *Q*-, and later the *Z*-, type of sensitizing for infrared photography, the spectroscopy section of the National Bureau of Standards tested the new plates by exploring arc-emission spectra in regions which had never been photographed before. In the case of tin, many new lines were thus discovered, and about 30 lines which had been observed hitherto only with bolometers and thermopiles were now photographed and measured with greater accuracy. Upon the completion of a new description of the infrared spectrum of tin, the published term analyses were examined to see how many of the observed lines could be explained as combinations of known terms. It was disappointing to find that so simple a spectrum as that of tin had such an incomplete and inaccurate term analysis. Serious discrepancies among the data and interpretations of different workers arose apparently from unreliable descriptions, so it was decided to reobserve the entire spectrum with more care. The arc spectrum of pure tin was accordingly photographed and measured from its limit in the ultraviolet below 1700 A to wavelengths approaching 13000 A in the infrared. A preliminary account of this investigation was presented at a meeting of the Optical Society of America in February

1939 [1],[1] and a complete report on this new description and analysis of the Sn I spectrum is the purpose of the present paper.

References to 81 publications on the spectra of tin previous to 1912 have been compiled and reviewed by H. Kayser [2]. In the 27 years which have elapsed since then, more than 60 papers dealing with tin spectra have appeared; but only those which are considered most relevant to the description and analysis of the first spectrum of tin will be mentioned here. It is interesting to note that the first extensive measurements of tin arc spectra were made by Kayser and Runge [3] in 1894. They measured the wavelengths of 73 tin arc lines (5631.91 to 2053.8 A) on Rowland's scale and discovered the first significant regularities in this spectrum. The arc spectrum of tin was first measured relative to international secondary standards in 1914 by Arnolds [4], who published wavelength values for 66 lines (6149.620 to 2194.42 A). Data for 49 lines among longer waves (9146.3 to 5631.70 A) were supplied in 1928 by Walters [5]. Infrared data for 24 lines (13022.0 to 8554.7 A) first observed with bolometers by Randall [6] in 1911 were revised and extended to 45 lines (24740.0 to 9852.1 A), 20 years later, by Randall and Wright [7], who, working with an 80-ampere arc between a carbon rod and a tin pool, observed the spectrum with thermopiles and a large grating spectrometer.

Tin arc spectra in the extreme ultraviolet were studied by McLellan, Young, and McLay [8], who photographed a 2-ampere arc to 1885 A with a small quartz spectrograph and recorded arc reversals from 1911 to 1756 A with a fluorite spectrograph exposed to tin in a carbon arc operated with 20 to 25 amperes. They admitted that their wavelength measurements might contain errors of ± 0.3 A. As a consequence, deviations of 10 or more wave numbers were tolerated in so-called "constant differences," and many spurious levels and false classifications resulted. These unreliable data have frequently been quoted and analyzed by others attempting to further the classification of tin lines, but to this date no one has published improved wavelengths for extreme ultraviolet arc lines of tin. The absorption spectrum of tin has been studied by many, but most thoroughly by Zumstein [9], who observed 53 absorption lines in the ultraviolet. However, the extreme ultraviolet wavelengths are quoted from McLennan et al. [8].

The Zeeman effect of tin lines has been observed by Back [10] and by Green and Loring [11]. The former observed 26 lines (2334 to 5632 A) and the latter 33 lines (2269 to 5632 A). These two sets of data are in excellent agreement; they are of utmost importance for making quantum identifications of certain spectral terms.

Further comments on publications dealing with tin spectra will be given below in connection with the discussion of my results.

II. EXPERIMENTS

Conventional arcs (and sparks) at atmospheric pressure were employed as light sources in making this new description of the Sn I spectrum. Arcs were operated on a d–c circuit with 220 volts applied potential, and with series resistance to regulate the current between 6 and 12 amperes. On account of the low melting point of tin (232° C), it was not possible to use solid electrodes in this arc, so lumps of pure

[1] Figures in brackets indicate the literature references at the end of this paper.

tin were burned in an arc having a pure copper rod (6 mm in diam) as upper electrode and a pool of molten tin in a cupped lower electrode of copper (12 mm in diam). Throughout the visible and ultraviolet spectra to 2000 A, comparison spark spectra of tin were made, so that any lines belonging to ionized atoms which might appear on the arc spectrograms could be recognized and removed from the final list of Sn I lines. These spark spectra were produced with solid tin electrodes in the secondary circuit of a transformer rated at 30,000 volts, with capacitors of 0.006 μf in parallel. The extreme ultraviolet spectrograms were made at Princeton University by A. G. Shenstone, who used an arc of 1 to 4 amperes between water-cooled electrodes of pure tin, or tin versus copper, in an atmosphere of pure nitrogen.

Descriptions of spectrographs and spectral intervals investigated with each are summarized as follows: Shenstone recorded the interval 1400 to 2200 A on Schumann plates with a normal-incidence vacuum spectrograph [12] having a 2-m glass grating ruled 30,000 lines to the inch. The dispersion is 4.2 A/mm and the definition and resolving power are superb. Nine exposures were made ranging in time from 20 minutes to 2½ hours.

At the National Bureau of Standards most of the spectrograms were made with stigmatic concave-grating spectrographs [13]. An aluminized Pyrex grating (22 ft in radius) ruled 30,000 lines per inch by R. W. Wood [14] was used in the first order from 2000 to 8200 A, and in the second order from 2500 to 4300 A. The dispersion in the second order averages 1 A/mm. The near infrared (7600 to 8900 A) was observed with an aluminized speculum grating originally ruled by H. A. Rowland with 20,000 lines per inch. The scale of these spectrograms was 3.5 A/mm. The entire infrared photographically accessible (7600 to 13000 A) was explored with a speculum grating ruled by J. A. Anderson; it has 7,500 lines per inch and gives a scale of 10 A/mm. A portion of the ultraviolet (2100 to 2700 A) was also observed with a large quartz Littrow spectrograph with dispersion ranging from 0.4 A/mm to 1.0 A/mm. Exposure times required to photograph the arc spectrum of tin varied from 1 or 2 minutes in the near ultraviolet to 4 hours for the longest waves recorded in the infrared.

Besides Schumann plates for recording the extreme ultraviolet, the following types of spectroscopic plates supplied by the Research Laboratory of the Eastman Kodak Co. [15] were used. Plates coated with No. 33 emulsion were employed in the range 2100 to 4800 A, *F*-sensitized plates from 4500 to 6800 A, *N*-sensitized from 6500 to 8200 A, *R-P*-sensitized from 7600 to 8900 A, *Q*-sensitized from 8000 to 11000 A, and *Z*-sensitized from 10000 to 13000 A.

The wavelengths (2100 to 8600 A) were obtained by interpolation between iron lines, the iron arc spectrum being photographed adjacent to tin on all spectrograms except those in the extreme ultraviolet which had sufficient lines of Cu, C, and N to fix the scale and corrections for each exposure. The wavelengths reported here are based on international secondary standards [16] or on interferometer values of iron and copper lines by Burns and Walters [17], supplemented in the extreme ultraviolet (1656 to 1930 A) by values of C and N lines recommended as tentative standards by Boyce and Robinson [18]. In the infrared and ultraviolet, outside the present limits of international secondary standards (6700 to 2500 A), interferometer values of iron lines measured at the National Bureau of

Standards [19] were relied upon. The first-order grating spectrum of tin beyond 8600 A was usually derived from iron lines in the second or third order, doubling or trebling the interpolated values of the apparent wavelengths of tin lines. (See fig. 1.)

On the Sn-Cu spectrograms made by Shenstone the Cu lines could be recognized by their enhancement at one electrode, and tin spark lines (Sn II) were likewise distinguished by enhancement at one end of the slit images. (See fig. 2.)

All spectrograms were measured, both direct and reversed, on comparators reading to 0.001 mm, and all lines were observed on four to six spectrograms except the faintest, which were discarded unless seen on at least two exposures. The grating spectrograms were reduced on the assumption of linear dispersion, and the prism spectrograms by aid of the Hartmann dispersion formula, corrections on account of variable dispersion being determined in every case from standards. Even under the best conditions, it is difficult to determine the wavelengths of tin lines within 0.01 A, because almost all of the line images are either hazy, wide, and unsymmetrical, or wide and more or less self-reversed. However, the agreement between different spectrographs and between successive spectrograms on each, and especially the analysis of spectral structure reported below, indicate that the goal of improving the description of the first spectrum of tin has been attained.

Portions of typical spectrograms are reproduced in figures 1 and 2.

III. RESULTS

1. WAVELENGTHS OF Sn I LINES

Data for 378 lines characteristic of neutral tin atoms are presented in table 1, where wavelengths, relative intensities, vacuum wave numbers, term combinations of classified lines, and residuals ($\nu_{obs.}-\nu_{calc.}$) appear in successive columns. Wave numbers for lines between 2000 and 10000 A were taken from Kayser's Tabelle der Schwingungszahlen [20]. For longer waves the values were first corrected to vacuum by extrapolating the dispersion formula of Meggers and Peters [21] and then computing reciprocals. Since the wavelengths shorter than 2000 A are vacuum values, the corresponding wave numbers are direct reciprocals of the observed wavelengths.

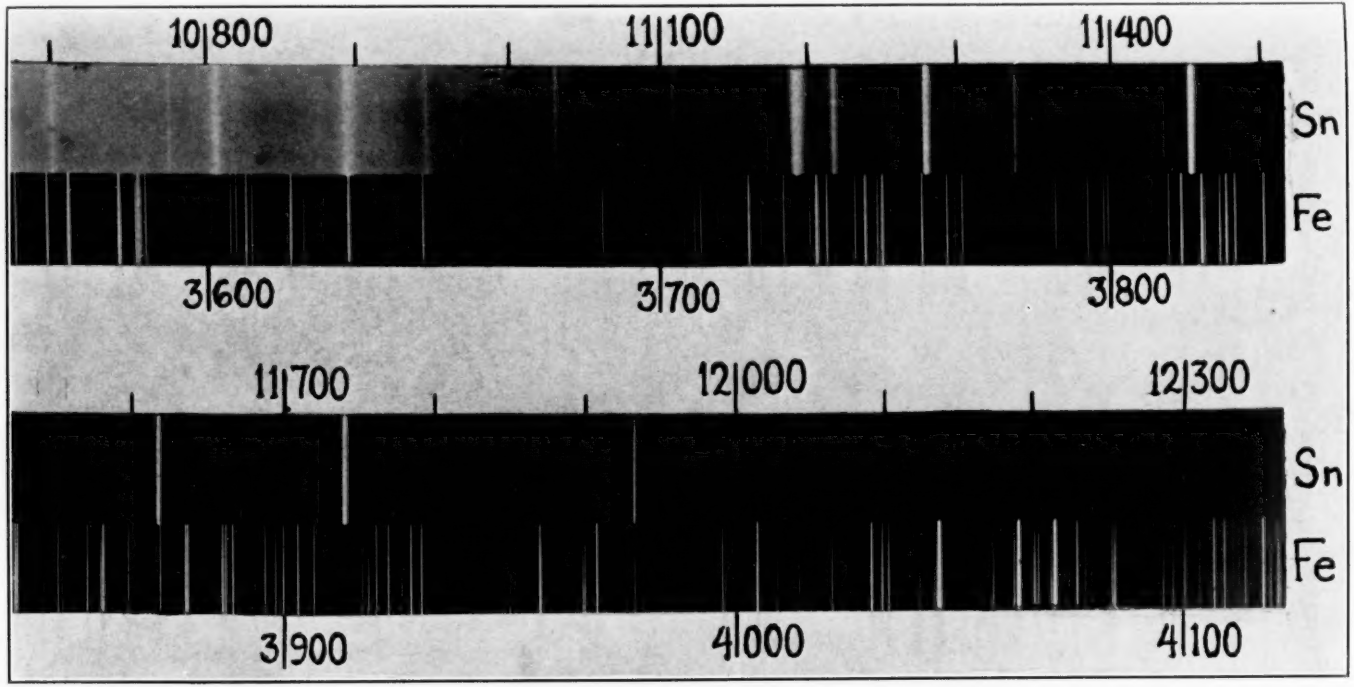

FIGURE 1.—*Portion of infrared arc spectrum of tin.*

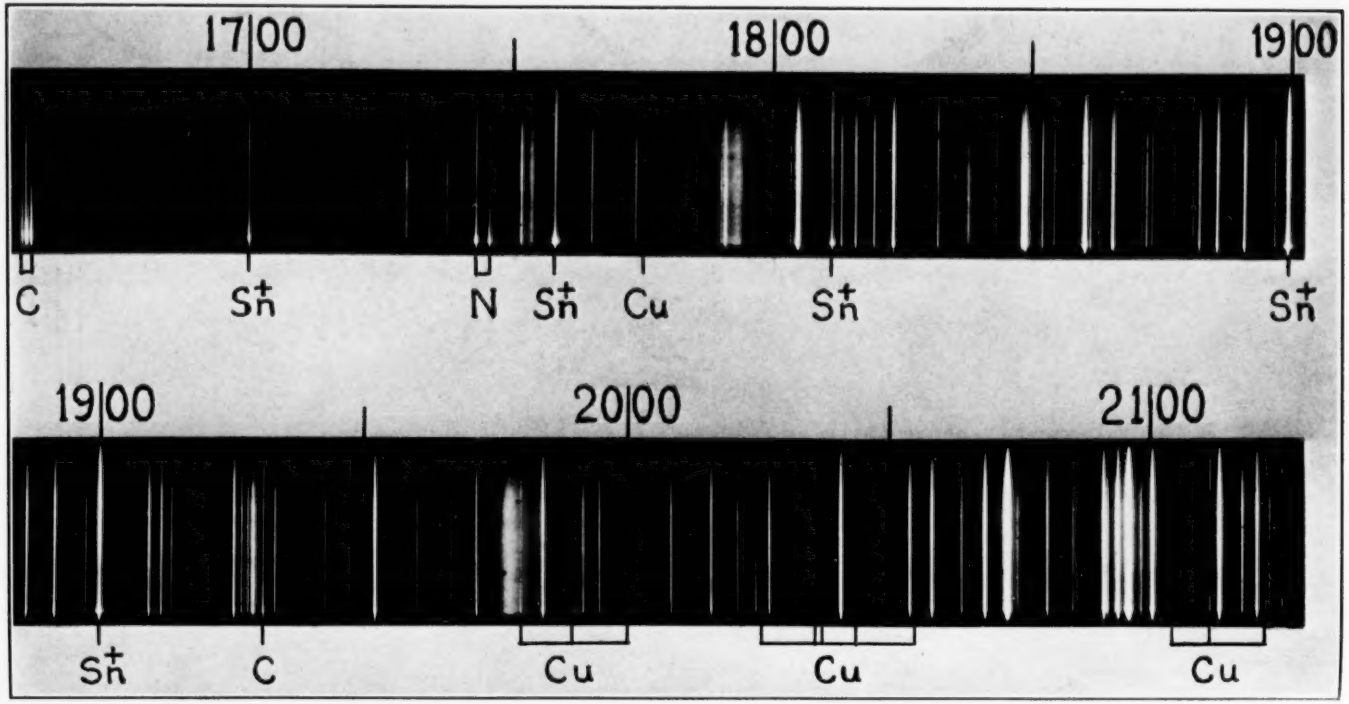

FIGURE 2.—*Extreme ultraviolet arc spectrum of tin.*

TABLE 1.—*First spectrum of tin* (Sn I)

λ_{air}A	Intensity and character	ν_{vac}cm^{-1}	Combination	$\nu_{obs.}-\nu_{calc.}$ 0.1 cm^{-1}
24738. 2	[40]	4041. 2		
24327. 2	[40]	4109. 5	$6s\ ^1P_1^\circ - 6p\ ^3P_1$	−19
22997. 2	[30]	4347. 2		
22131. 7	[40]	4517. 2	$6p\ ^1D_2 - 7s\ ^1P_1^\circ$	+1
21686. 2	[80]	4610. 0	$6p\ ^3S_1 - 7s\ ^3P_2^\circ$	0
20861. 7	[400]	4792. 2	$6p\ ^3P_0 - 7s\ ^3P_1^\circ$	+1
20622. 2	[200]	4847. 8	$6p\ ^3P_1 - 7s\ ^3P_0^\circ$	+1
20594. 4	[70]	4854. 4	$6p\ ^3P_1 - 7s\ ^3P_1^\circ$	+8
17807. 5	[100]	5614. 1	$6p\ ^3P_1 - 5d\ ^3P_1^\circ$	+6
17744. 7	[70]	5633. 9		
17198. 8	[40]	5812. 8	$6p\ ^1P_1 - 7s\ ^3P_2^\circ$	+5
17019. 9	[100]	5873. 9	$6p\ ^3D_1 - 7s\ ^3P_0^\circ$	0
17000. 5	[200]	5880. 6	$6p\ ^3D_1 - 7s\ ^3P_1^\circ$	+8
16381. 2	[70]	6102. 9	$6p\ ^1P_1 - 7s\ ^1P_1^\circ$	−5
15793. 7	[30]	6329. 9		
15749. 7	[70]	6347. 6		
15635. 2	[100]	6394. 1		
15584. 2	[50]	6415. 0	$6p\ ^1P_1 - 8s\ ^3P_1^\circ$	−22
15464. 2	[300]	6464. 8	$6p\ ^1D_2 - 6d\ ^3P_2^\circ$	+11
15367. 2	[100]	6505. 6	$5d\ ^1F_3^\circ - 2754$	−13
15055. 2	[100]	6640. 4	$6p\ ^3D_1 - 5d\ ^3P_1^\circ$	+7
15018. 2	[130]	6656. 8	$5d\ ^1F_3^\circ - 2605$	+6
14797. 2	[60]	6756. 2	$6p\ ^3P_1 - 5d\ ^1P_1^\circ$	−12
14668. 2	[100]	6815. 6		
14482. 2	[100]	6903. 1		
13608. 2	[*1440*]	7346. 5	$6s\ ^1P_1^\circ - 6p\ ^1P_1$	+2
13460. 2	[*3780*]	7427. 3	$6s\ ^3P_1^\circ - 6p\ ^3D_1$	−8
13349. 2	[30]	7489. 1	$6p\ ^3S_1 - 6d\ ^1D_2^\circ$	−13
13320. 9	[70]	7505. 0	$5d\ ^3P_1^\circ - 2668$	+5
13081. 5	[*675*]	7642. 3	$6p\ ^3P_1 - 6d\ ^3D_2^\circ$	+3
13018. 5	[*1870*]	7679. 2	$6p\ ^1S_0 - 6s\ ^1P_1^\circ$?	0
13000. 3	[200]	7690. 0	$5d\ ^3F_3^\circ - 6891$	+24
12981. 7	[*1870*]	7701. 0	$6s\ ^3P_0^\circ - 6p\ ^3D_1$	−5
12934. 2	[30]	7729. 3		
12888. 5	[*890*]	7756. 7	$5d\ ^3D_1^\circ - 6891$	+17
12845. 2	[*160*]	7782. 9	$6p\ ^3D_1 - 5d\ ^1P_1^\circ$	−7
12788. 2	[*370*]	7817. 6	$5d\ ^3P_2^\circ - 2668$	+6
12536. 5	1[425]	7974. 5	$6s\ ^3P_2^\circ - 6p\ ^1P_1$	−1
12530. 87	1[425]	7978. 11	$6s\ ^1P_1^\circ - 6p\ ^3P_2$	0
12335. 6	2[*330*]	8104. 4	$5d\ ^3F_3^\circ - 6906$	0
12313. 24	4[*1110*]	8119. 11	$5d\ ^3F_2^\circ - 6891$	0
12054. 5	1[30]	8293. 4		
12009. 50	3[*480*]	8324. 47	$6s\ ^3P_1^\circ - 6p\ ^3D_2$ $6p\ ^3P_0 - 6d\ ^3F_2^\circ$	0 0
11932. 99	30[*2540*]	8377. 84	$6s\ ^3P_2^\circ - 6p\ ^3D^3$	−2
11835. 82	4[*1060*]	8433. 79		
11848. 04	2	8437. 91	$6p\ ^3S_1 - 2911$	−1
11825. 18	10[*960*]	8454. 22	$6s\ ^3P_1^\circ - 6p\ ^3P_1$	−1
11739. 78	80[*2580*]	8515. 72	$6s\ ^3P_1^\circ - 6p\ ^3P_0$ $6p\ ^3D_2 - 6d\ ^3F_2^\circ$	−1 +1
11694. 45	3[*250*]	8548. 72	$6s\ ^1P_1^\circ - 6p\ ^3S_1$	+1
11670. 77	10[*760*]	8566. 07	$5d\ ^3D_2^\circ - 6906$	+1
11650. 76	3[125]	8580. 78	$5d\ ^3D_2^\circ - 6891$	0
11648. 32	2	8582. 58		
11616. 26	60[*2000*]	8606. 27	$6s\ ^3P_2^\circ - 6p\ ^3P_2$	−1
11533. 4	2*h*[30]	8668. 1	$6p\ ^3D_1 - 6d\ ^3D_2^\circ$	−1
11500. 9	2*h*	8692. 6	$6p\ ^1P_1 - 6d\ ^1D_2^\circ$	−1

TABLE 1.—*First spectrum of tin* (Sn I)—Continued

λ_{air}A	Intensity and character	ν_{vac}cm^{-1}	Combination	$\nu_{obs.}-\nu_{calc.}$ 0.1 cm^{-1}
11454. 59	150[*2000*]	8727. 74	$6s\ ^3P_0^\circ-6p\ ^3P_1$	0
11336. 97	15*h*[*170*]	8818. 29	$6p\ ^3D_1-6d\ ^3F_2^\circ$	+4
11277. 66	150[*560*]	8864. 66		
11222. 50	3*h*	8908. 23	$5d\ ^3D_3^\circ-2759$	+3
11216. 73	15*h*[80]	8912. 81	$5d\ ^3D_3^\circ-2754$	+2
11191. 85	200[*700*]	8932. 63	$6s\ ^1P_1^\circ-6p\ ^1D_2$	0
11109. 98	6*h*	8998. 45	$5d\ ^3D_3^\circ-2668$	0
11032. 04	7	9062. 03	$5d\ ^3D_3^\circ-2605$	+1
10946. 64	5*h*[30]	9132. 72	$6p\ ^3D_1-6d\ ^3D_1^\circ$	−1
10932. 13	1	9144. 85	$5d\ ^3D_3^\circ-2522$	0
10922. 73	1*h*	9152. 71	$5d\ ^1F_3^\circ-108$	0
10894. 00	250[*540*]	9176. 85	$6s\ ^3P_2^\circ-6p\ ^3S_1$ $6p\ ^3D_2-7s\ ^3P_2^\circ$	0 +1
10817. 73	2	9241. 55		
10807. 58	50[*110*]	9250. 23	$5d\ ^1D_2^\circ-2759$	−1
10776. 76	4	9276. 69	$6p\ ^3P_0-7s\ ^1P_1^\circ$	−1
10702. 9	1	9340. 7	$5d\ ^1D_2^\circ-2668$	+1
10700. 56	5*h*[30]	9342. 75	$5d^1\ D_2^\circ-2666$	0
10467. 40	3	9550. 86		
10456. 47	80[*250*]	9560. 84	$6s\ ^3P_2^\circ-6p\ ^1D_2$	−1
10424. 06	5*h*	9590. 57	$6p\ ^3P_0-8s\ ^3P_1^\circ$	0
10357. 64	3*h*	9652. 06	$6p\ ^3P_1-8s\ ^3P_1^\circ$	0
10187. 44	6*h*	9813. 32		
10083. 3	5*h*	9914. 6	$6p\ ^3P_2-8s\ ^3P_2^\circ$	−3
9856. 26	10	10143. 06	$6p\ ^3D_3-8s\ ^3P_2^\circ$	−2
9850. 52	500*l*	10148. 97		
9837. 5	2	10162. 4	$6p\ ^3P_0-7d\ ^3D_1^\circ$	+2
9814. 3	4*h*	10186. 4	$5d\ ^3F_3^\circ-4392$	−1
9805. 38	300*Hl*	10195. 69	$5d\ ^3F_3^\circ-4383$	0
9799. 94	5	10201. 35	$6p\ ^3P_0-6d\ ^3F_2^\circ$	0
9778. 3	2	10223. 9	$6p\ ^3P_1-7d\ ^3D_1^\circ$	+2
9742. 8	100*Hl*	10261. 2		
9741. 1	50+*H*	10263. 0	$6p\ ^3P_1-6d\ ^3F_2^\circ$ $5d\ ^3D_1^\circ-4383$	+1 0
9616. 40	150*h*	10396. 05		
9451. 78	10*h*	10577. 12		
9415. 37	80*Hl*	10618. 02	$5d\ ^3F_2^\circ-4392$	0
9410. 86	50*Hl*	10623. 11	$5d\ ^3F_3^\circ-4387$	0
9362. 21	20*h*	10678. 31	$6p\ ^3D_1-8s\ ^3P_1^\circ$	0
9272. 5	10*h*	10781. 6	$6p\ ^3P_0-4943$	−1
9219. 9	1	10843. 1	$6p\ ^3P_1-4943$	−1
9145. 1	20*H*	10931. 8		
9092. 1	1	10995. 5	$5d\ ^3F_2^\circ-7p\ ^3D_3$	+2
9023. 07	20*H*	11079. 66	$5d\ ^3D_3^\circ-4392$	+1
9018. 95	30*H*	11084. 72	$5d\ ^3D_2^\circ-4387$	−1
8907. 6	20*H*	11223. 3	$6p\ ^3P_0-6d\ ^3P_2^\circ$	−1
8886. 3	7*h*	11250. 2	$6p\ ^3D_1-7d\ ^3D_1^\circ$	+3
8812. 6	10*Hl*	11344. 3	$6p\ ^3P_1-4442$	0
8708. 3	20*Hw*	11480. 2		
8694. 13	5*h*	11498. 86	$6s\ ^1P_1^\circ-7p\ ^3D_1$	+2
8681. 7	50*Hw*	11515. 3		
8649. 3	20*Hl*	11558. 5	$5d\ ^3D_3^\circ-108$	−1
8552. 60	400	11689. 14	$6s\ ^3P_1^\circ-6p\ ^1P_1$	−1
8525. 6	6*H*	11726. 2	$6p\ ^3P_0-9s\ ^3P_1^\circ$	0
8499. 3	3*H*	11762. 4		
8458. 04	5*h*	11819. 83	$5d\ ^3F_3^\circ-2759$	−1
8454. 74	6*h*	11824. 44	$5d\ ^3F_3^\circ-2754$	−2

TABLE 1.—*First spectrum of tin* (Sn I)—Continued

λ_{air}A	Intensity and character	ν_{ac}cm^{-1}	Combination	$\nu_{obs.}-\nu_{calc.}$ 0.1 cm^{-1}
8432. 14	5*h*	11856. 13	$6s\ ^1P_1^\circ-7p\ ^3P_1$	−1
8422. 72	300*hl*	11869. 39	$6p\ ^3D_1-4943$	0
8393. 83	4*h*	11910. 24	$5d\ ^3F_3^\circ-2668$	−2
8391. 31	20*h*	11913. 82	$6s\ ^1P_1^\circ-7p\ ^3D_2$	+1
8381. 69	4*h*	11927. 49	$6p\ ^3P_1-6d\ ^1D_2^\circ$	−1
8357. 04	80	11962. 68	$6s\ ^3P_0^\circ-6p\ ^1P_1$	+1
8349. 35	30*h*	11973. 70	$5d\ ^3F_3^\circ-2605$	−2
8345. 23	10*h*	11979. 60	$5d\ ^3D_1^\circ-2666$	−1
8338. 6	10*Hw*	11989. 1		
8250. 03	8*h*	12117. 84	$6s\ ^1P_1^\circ-7p\ ^3P_0$	+1
8247. 22	2*h*	12121. 96		
8245. 84	4*h*	12124. 00	$5d\ ^3D_1^\circ-2522$	−1
8243. 8	1*h*	12127. 0	$6s\ ^3P_2^\circ-7p\ ^3D_1$	0
8160. 08	2*h*	12251. 42	$5d\ ^3F_2^\circ-2759$	0
8133. 2	10*Hw*	12291. 9		
8121. 0	30*Hl*	12310. 4	$6p\ ^3D_1-6d\ ^3P_2^\circ$	−7
8114. 09	200	12320. 86	$6s\ ^3P_1^\circ-6p\ ^3P_2$	−1
8100. 25	3*h*	12341. 91	$5d\ ^3F_2^\circ-2668$	0
8046. 8	5*Hl*	12423. 9		
8039. 3	30*Hl*	12435. 5		
8030. 5	100*Hl*	12449. 10		
8007. 7	1*h*	12484. 5	$6s\ ^3P_2^\circ-7\ ^3P_1$	0
8005. 29	7*h*	12488. 31	$5d\ ^3F_3^\circ-2522$	0
7971. 02	8*h*	12542. 0	$6s\ ^3P_2^\circ-7p\ ^3D_2$	0
7910. 46	10*h*	12638. 02		
7903. 52	2*h*	12649. 12		
7863. 74	8*h*	12713. 10	$5d\ ^3P_2^\circ-2759$	+1
7852. 6	2*H*	12731. 1	$6p\ ^3D_1-6d\ ^3P_1^\circ$	−6
7817. 2	4*H*	12788. 8		
7808. 23	10*h*	12803. 48	$5d\ ^3D_2^\circ-2668$	0
7807. 0	2*H*	12805. 5	$5d\ ^3D_2^\circ-2666$	0
7801. 8	8*H*	12814. 0	$6p\ ^3D_1-9s\ ^3P_1^\circ$	+1
7769. 2	3*H*	12867. 8	$5d\ ^3D_2^\circ-2605$	+8
7754. 97	100	12891. 41	$6s\ ^3P_1^\circ-6p\ ^3S_1$	−1
7741. 43	3	12913. 96		
7719. 93	3*h*	12949. 92		
7717. 57	2*h*	12953. 89	$6p\ ^3D_1-6d\ ^1D_2^\circ$	+1
7685. 30	30*h*	13008. 28	$6s\ ^1P_1^\circ-7p\ ^1S_0$	+1
7627. 4	4*H*	13107. 0		
7626. 4	5*H*	13108. 8		
7593. 85	2	13164. 93	$6s\ ^3P_0^\circ-6p\ ^3S_1$	0
7530. 7	1	13275. 3	$6s\ ^3P_1^\circ-6p\ ^1D_2$	−2
7398. 6	20*H*	13512. 4		
6898. 50	2	14491. 91		
6462. 07	4	15470. 65		
6444. 85	5*H*	15512. 0		
6354. 35	40*h*	15732. 91	$6s\ ^1P_1^\circ-7p\ ^1P_1$	0
6310. 78	100*hl*	15841. 53	$6s\ ^3P_1^\circ-7p\ ^3D_1$	−1
6275. 75	5*h*	15929. 95	$6s\ ^1P_1^\circ-7p\ ^3P_2$	+1
6203. 64	20*hl*	16115. 12	$6s\ ^3P_0^\circ-7p\ ^3D_1$	+1
6203. 01	3*h*	16116. 76	$6s\ ^1P_1^\circ-7p\ ^3S_1$	+1
6171. 50	150*h*	16199. 04	$6s\ ^3P_1^\circ-7p\ ^3P_1$	−1
6154. 60	200*hl*	16243. 52	$6s\ ^1P_1^\circ-7p\ ^1D_2$	0
6149. 71	400*hs*	16256. 44	$6s\ ^3P_1^\circ-7p\ ^3D_2$	−2
6110. 38	4*h*	16361. 08	$6s\ ^3P_2^\circ-7p\ ^1P_1$	−1

TABLE 1.—*First spectrum of tin* (Sn I)—Continued

λ_{air}A	Intensity and character	ν_{vac}cm^{-1}	Combination	$\nu_{obs.}-\nu_{calc.}$ 0.1 cm^{-1}
6073. 46	100*hl*	16460. 53	$6s\ ^3P_1^\circ - 7p\ ^3P_0$	−1
6069. 00	250*hs*	16472. 63	$6s\ ^3P_0^\circ - 7p\ ^3P_1$	+1
6060. 75	4*h*	16495. 05		
6054. 86	200*hl*	16511. 10	$6s\ ^3P_2^\circ - 7p\ ^3D_3$	0
6037. 70	150*hl*	16558. 02	$6s\ ^3P_2^\circ - 7p\ ^3P_2$	−1
6010. 96	4*H*	16631. 68		
5970. 30	100*h*	16774. 95	$6s\ ^3P_2^\circ - 7p\ ^3S_1$	0
5925. 44	50*hl*	16871. 72	$6s\ ^3P_2^\circ - 7p\ ^1D_2$	−1
5801. 81	10*h*	17231. 23	$6s\ ^1P_1^\circ - 2666$	−2
5761. 76	10*h*	17351. 01	$6s\ ^3P_1^\circ - 7p\ ^1S_0$	−1
5753. 59	15*h*	17375. 64	$6s\ ^1P_1^\circ - 2522$	−2
5631. 707	500	17751. 69	$5p\ ^1S_0 - 6s\ ^3P_0^\circ$	+1
5176. 98	5*h*	19310. 92		
5174. 54	20*h*	19320. 02		
5160. 24	10*h*	19373. 56		
4979. 73	20*h*	20075. 83	$6s\ ^3P_1^\circ - 7p\ ^1P_1$	0
4931. 37	10*h*	20272. 70	$6s\ ^3P_1^\circ - 7p\ ^3P_2$	0
4912. 82	3*h*	20349. 24	$6s\ ^3P_0^\circ - 7p\ ^1P_1$	0
4886. 36	2*h*	20459. 44	$6s\ ^3P_1^\circ - 7p\ ^3S_1$	−2
4766. 22	5*H*	20975. 14		
4633. 93	3*h*	21573. 93		
4524. 744	1000	22094. 52	$5p\ ^1S_0 - 6s\ ^1P_1^\circ$	0
3801. 022	2000*R*	26301. 26	$5p\ ^1D_2 - 6s\ ^3P_1^\circ$	+1
3655. 778	250	27346. 20	$5p\ ^1S_0 - 5d\ ^3D_1^\circ$	0
3330. 620	500*r*	30015. 84	$5p\ ^1D_2 - 6s\ ^3P_2^\circ$	0
3262. 340	2500*R*	30644. 04	$5p\ ^1D_2 - 6s\ ^1P_1^\circ$	−1
3223. 572	10	31012. 57	$5p\ ^1D_2 - 19529$	+1
3218. 707	40	31059. 44	$5p\ ^1S_0 - 7s\ ^3P_1^\circ$	−1
3175. 046	2000*R*	31486. 53	$5p\ ^3P_2 - 6s\ ^3P_1^\circ$	0
3141. 836	60	31819. 34	$5p\ ^1S_0 - 5d\ ^3P_1^\circ$	−1
3034. 120	900*R*	32948. 92	$5p\ ^3P_1 - 6s\ ^3P_0^\circ$	−1
3032. 805	200*h*	32963. 21	$5p\ ^1S_0 - 5d\ ^1P_1^\circ$	−1
3009. 136	700*R*	33222. 48	$5p\ ^3P_1 - 6s\ ^3P_1^\circ$	+1
2913. 543	200*h*	34312. 45	$5p\ ^1S_0 - 6d\ ^3D_1^\circ$	0
2863. 324	600*R*	34914. 22	$5p\ ^3P_0 - 6s\ ^3P_1^\circ$	0
2850. 62	200*r*	35069. 8	$5p\ ^1D_2 - 5d\ ^3D_2^\circ$	−2
2839. 99	700*R*	35201. 1	$5p\ ^3P_2 - 6s\ ^3P_2^\circ$	0
2813. 575	80	35531. 53	$5p\ ^1D_2 - 5d\ ^3F_2^\circ$	−1
2812. 59	60	35544. 0	$5p\ ^1S_0 - 7s\ ^1P_1^\circ$	−2
2790. 18	4	35829. 4	$5p\ ^3P_2 - 6s\ ^1P_1^\circ$	0
2787. 96	60	35858. 0	$5p\ ^1S_0 - 8s\ ^3P_1^\circ$	0
2785. 030	80	35895. 69	$5p\ ^1D_2 - 5d\ ^3D_1^\circ$	−1
2779. 810	150	35963. 09	$5p\ ^1D_2 - 5d\ ^3F_3^\circ$	0
2761. 78	20	36197. 9	$5p\ ^3P_2 - 19529$	+1
2744. 19	2*h*	36429. 9	$5p\ ^1S_0 + 7d\ ^3D_1^\circ$	+3
2706. 510	1000*R*	36937. 02	$5p\ ^3P_1 - 6s\ ^3P_2^\circ$	0
2661. 243	200*R*	37565. 27	$5p\ ^3P_1 - 6s\ ^1P_1^\circ$	0
2636. 94	50*H*	37911. 5	$5p\ ^1S_0 - 6d\ ^3P_1^\circ$	+1
2635. 396	3	37933. 67	$5p\ ^3P_1 - 19529$	0
2631. 28	7*H*	37993. 0	$5p\ ^1S_0 - 9s\ ^3P_1^\circ$	−6
2594. 424	200*r*	38532. 69	$5p\ ^1D_2 - 5p\ ^1D_2^\circ$	0
2588. 411	7*h*	38622. 20	$5p\ ^1D_2 - 11919$	0
2571. 576	500*R*	38875. 02	$5p\ ^1D_2 - 5d\ ^3D_3^\circ$	0
2558. 01	40*H*	39081. 2	$5p\ ^1S_0 - 2911$	+1
2548. 53	5*h*	39226. 5	$5p\ ^1S_0 - 10s\ ^3P_1^\circ$	−2

TABLE 1.—*First spectrum of tin* (Sn I)—Continued

λ_{air}A	Intensity and character	ν_{vac}cm^{-1}	Combination	$\nu_{obs.}-\nu_{calc.}$ 0.1 cm^{-1}
2546. 549	400*r*	39257. 05	$5p\,^3P_0-6s\,^1P_1^\circ$	0
2532. 87	5*H*	39469. 0		
2531. 17	80*Hl*	39495. 6	$5p\,^1S_0-6d\,^1P_1^\circ$	+2
2523. 915	90*r*	39609. 08	$5p\,^1D_2-7s\,^3P_1^\circ$	0
2499. 11	5*h*	40002. 2		
2495. 704	200*r*	40056. 78	$5p\,^1D_2-5d\,^3P_2^\circ$	+2
2491. 78	10*h*	40119. 8	$5p\,^1S_0-8s\,^1P_1^\circ$	+1
2483. 392	300*r*	40255. 35	$5p\,^3P_2-5d\,^3D_2^\circ$	0
2476. 395	20	40369. 08	$5p\,^1D_2-5d\,^3P_1^\circ$	+1
2455. 235	60	40716. 97	$5p\,^3P_2-5d\,^3F_2^\circ$	+1
2433. 467	15	41081. 16	$5p\,^3P_2-5d\,^3D_1^\circ$	+1
2429. 488	1000*R*	41148. 44	$5p\,^3P_2-5d\,^3F_3^\circ$	0
2421. 697	800*R*	41280. 85	$5p\,^1D_2-5d\,^1F_3^\circ$	0
2408. 15	100	41513. 0	$5p\,^1D_2-5d\,^1P_1^\circ$	+1
2398. 71	3*h*	41676. 4		
2386. 96	10*Hw*	41881. 5		
2380. 72	60	41991. 3	$5p\,^3P_1-5d\,^3D_2^\circ$	+1
2357. 896	20*h*	42397. 71	$5p\,^1D_2-6d\,^3D_2^\circ$	+2
2354. 837	1000*R*	42452. 78	$5p\,^3P_1-5d\,^3F_2^\circ$	0
2334. 80	300*R*	42817. 1	$5p\,^3P_1-5d\,^3D_1^\circ$	+1
2332. 35	6*h*	42862. 0	$5p\,^1D_2-6d\,^3D_1^\circ$	−1
2317. 23	600*R*	43141. 7	$5p\,^1D_2-6d\,^3F_3^\circ$	+2
2290. 66	2*h*	43642. 1		
2286. 681	200*R*	43717. 97	$5p\,^3P_2-5d\,^1D_2^\circ$	0
2282. 257	20	43802. 72	$5p\,^1D_2-7s\,^3P_2^\circ$	0
2282. 01	2*h*	43807. 5	$5p\,^3P_2-11919$	0
2268. 913	400*R*	44060. 31	$5p\,^3P_2-5d\,^3D_3^\circ$	0
2267. 186	30*r*	44093. 87	$5p\,^1D_2-7s\,^1P_1^\circ$	+1
2251. 168	60*r*	44407. 59	$5p\,^1D_2-8s\,^3P_1^\circ$	0
2246. 048	400*R*	44508. 80	$5p\,^3P_0-5d\,^3D_1^\circ$	0
2233. 35	7*h*	44761. 8		
2231. 725	80*R*	44794. 43	$5p\,^3P_2-7s\,^3P_1^\circ$	0
2222. 555	6*h*	44979. 23	$5p\,^1D_2-7d\,^3D_1^\circ$	0
2220. 623	10*h*	45018. 35	$5p\,^1D_2-7d\,^3F_2^\circ$	0
2211. 05	40*rs*	45213. 2	$5p\,^1D_2-7d\,^3F_3^\circ$	+2
2209. 650	400*R*	45241. 88	$5p\,^3P_2-5d\,^3P_2^\circ$	0
2199. 337	300*R*	45454. 01	$5p\,^3P_1-5d\,^1D_2^\circ$	+1
2194. 494	150*R*	45554. 31	$5p\,^3P_2-5d\,^3P_1^\circ$	0
2171. 32	80*rs*	46040. 4	$5p\,^1D_2-6d\,^3P_2^\circ$	0
2168. 522	2	46099. 84	$5p\,^1D_2-4442$	0
2162. 982	5	46217. 90	$5p\,^1D_2-4324$	0
2151. 43	20*R*	46466. 0	$5p\,^3P_2-5d\,^1F_3^\circ$	−1
2148. 733	40*Rs*	46524. 36	$5p\,^3P_1-7s\,^3P_0$	0
2148. 460	15*rs*	46530. 26	$5p\,^3P_1-7s\,^3P_1^\circ$	0
2147. 868	6	46543. 09	$5p\,^1D_2-9s\,^3P_1^\circ$	−1
2141. 434	20	46682. 91	$5p\,^1D_2-6d\,^1D_2^\circ$	−2
2140. 734	25*rs*	46698. 17	$5p\,^3P_2-5d\,^1P_1^\circ$	0
2127. 995	7	46977. 68	$5p\,^3P_1-5d\,^3P_2^\circ$	−1
2123. 62	7*h*	47074. 5	$5p\,^1D_2-3467$	+1
2121. 265	50*h*	47126. 7	$5p\,^1D_2-6d\,^3D_3^\circ$	0
2118. 38	10*h*	47190. 9	$5p\,^1D_2-3351$	+2
2113. 93	100*R*	47290. 2	$5p\,^3P_1-5d\,^3P_1^\circ$	0
2100. 934	100	47582. 71	$5p\,^3P_2-6d\,^3D_2^\circ$	−1
2098. 82	3	47630. 6	$5p\,^1D_2-2911$	−1
2096. 39	200*rl*	47685. 8	$5p\,^1D_2-6d\,^1F_3^\circ$	0

TABLE 1.—*First spectrum of tin* (Sn I)—Continued

λ_{air}A	Intensity and character	ν_{vac}cm^{-1}	Combination	$\nu_{obs.}-\nu_{calc.}$ 0.1 cm^{-1}
2094. 348	40	47732. 32	$5p\ ^3P_2-6d\ ^3F_2^\circ$	−2
2093. 82	3	47744. 4		
2092. 422	3	47776. 25	$5p\ ^1D_2-10s\ ^3P_1^\circ$	0
2091. 582	30*r*	47795. 44	$5p\ ^3P_1-5d\ ^3P_0$	0
2085. 62	5	47932. 0	$5p\ ^1D_2-2610$	+2
2080. 618	25	48047. 27	$5p\ ^3P_2-6d\ ^3D_1^\circ$	−1
2074. 87	4*H*	48180. 4		
2073. 08	100*r*	48222. 0	$5p\ ^3P_0-7s\ ^3P_1^\circ$	−1
2072. 89	100	48226. 4	$5p\ ^1D_2-2315$	−1
2068. 583	80	48326. 67	$5p\ ^3P_2-6d\ ^3F_3^\circ$	−1
2063. 998	20	48434. 11	$5p\ ^3P_1-5d\ ^1P_1^\circ$	0
2061. 57	1	48491. 1		
2059. 612	5	48537. 24	$5p\ ^1D_2-8s\ ^3P_2^\circ$	+1
2058. 31	70*h*	48567. 9		
2054. 03	50*h*	48669. 1	$5p\ ^1D_2-8s\ ^1P_1^\circ$	−2
2040. 905	20	48982. 07	$5p\ ^3P_0-5d\ ^3P_1^\circ$	+1
2040. 660	50	48987. 95	$5p\ ^3P_2-7s\ ^3P_2^\circ$	0
2028. 597	5	49279. 20	$5p\ ^3P_2-7s\ ^1P_1^\circ$	+1
2026. 975	30	49318. 64	$5p\ ^3P_1-6d\ ^3D_2^\circ$	−1
2020. 833	10	49468. 51	$5p\ ^3P_1-6d\ ^3F_2^\circ$	+1
2015. 764	30	49592. 89	$5p\ ^3P_2-8s\ ^3P_1^\circ$	0
2008. 048	25	49783. 4	$5p\ ^3P_1-6d\ ^3D_1^\circ$	+1
λ_{vac}A				
1994. 98	20	50125. 9	$5p\ ^3P_0-5d\ ^1P_1^\circ$	0
1993. 44	3	50164. 6	$5p\ ^3P_2-7d\ ^3D_1^\circ$	+1
1991. 885	15	50203. 7	$5p\ ^3P_2-7d\ ^3F_2^\circ$	0
1984. 20	80	50398. 2	$5p\ ^3P_2-7d\ ^3F_3^\circ$	−1
1977. 6	50*H*	50566.		
1971. 46	30	50723. 9	$5p\ ^3P_1-7s\ ^3P_2^\circ$	0
1969. 98	1	50761. 9	$5p\ ^1D_2-9s\ ^3P_2^\circ$	−1
1969. 125	4	50784. 0	$5p\ ^3P_2-4943$	0
1967. 49	5*H*	50826. 2		
1960. 21	15	51014. 9	$5p\ ^3P_1-7s\ ^1P_1^\circ$	−1
1952. 15	150*rs*	51225. 6	$5p\ ^3P_2-6d\ ^3P_2^\circ$	−1
1949. 88	1	51285. 2	$5p\ ^3P_2-4442$	+1
1948. 89	2	51311. 3	$5p\ ^3P_1-8s\ ^3P_0^\circ$	0
1948. 225	8	51328. 8	$5p\ ^3P_1-8s\ ^3P_1^\circ$	0
1945. 40	3	51403. 3	$5p\ ^3P_2-4324$	+1
1942. 686	20	51475. 1	$5p\ ^3P_0-6d\ ^3D_1^\circ$	0
1933. 17	25	51728. 5	$5p\ ^3P_2-9s\ ^3P_1^\circ$	0
1928. 9	40*HW*	51842.		
1927. 95	15	51868. 6	$5p\ ^3P_2-6d\ ^1D_2^\circ$	0
1926. 77	20	51900. 4	$5p\ ^3P_1-7d\ ^3D_1^\circ$	0
1925. 31	80*rs*	51939. 8	$5p\ ^3P_1-7d\ ^3F_2^\circ$	0
1913. 52	20	52259. 6	$5p\ ^3P_2-3467$	−1
1911. 61	40	52312. 0	$5p\ ^3P_2-6d\ ^3D_3^\circ$	0
1909. 30	50*h*	52375. 3		
1907. 40	3	52427. 5		
1904. 04	2	52519. 9	$5p\ ^3P_1-4943$	0
1897. 29	20	52706. 8	$5p\ ^3P_0-7s\ ^1P_1^\circ$	0
1891. 40	100*rl*	52871. 0	$5p\ ^3P_2-6d\ ^1F_3^\circ$	−1
1888. 16	3	52961. 6	$5p\ ^3P_1-6d\ ^3P_2^\circ$	0
			$5p\ ^3P_2-10s\ ^3P_1^\circ$	0
1886. 05	80*rs*	53020. 9	$5p\ ^3P_0-8s\ ^3P_1^\circ$	+3
1884. 24	2*h*	53071. 8		
1882. 64	30*h*	53117. 0	$5p\ ^3P_2-2610$	−1

TABLE 1.—*First spectrum of tin* (Sn I)—Continued

λ_{air} A	Intensity and character	ν_{vac} cm^{-1}	Combination	$\nu_{obs.}-\nu_{calc.}$ 0.1 cm^{-1}
1878. 63	5	53230. 3	$5p\ ^3P_2-6d\ ^1P_1^\circ$	0
1873. 29	15	53382. 1	$5p\ ^3P_1-6d\ ^3P_1^\circ$	−1
1872. 24	10*h*	53411. 9	$5p\ ^3P_2-2315$	+1
1871. 29	10	53439. 1		
1870. 40	1	53464. 5	$5p\ ^3P_1-9s\ ^3P_1^\circ$	+1
1865. 96	30*rs*	53592. 1	$5p\ ^3P_0-7d\ ^3D_1^\circ$	−1
1865. 52	20	53604. 3	$5p\ ^3P_1-6d\ ^1D_2^\circ$	0
1862. 93	7*h*	53679. 0		
1861. 42	20	53722. 4	$5p\ ^3P_2-8s\ ^3P_2^\circ$	0
1860. 32	200*Rs*	53754. 2		
1856. 82	2	53855. 5		
1854. 24	10	53930. 5		
1852. 00	30	53995. 6	$5p\ ^3P_1-3467$	0
1849. 49	10*R*	54069. 0		
1848. 75	50*R*	54090. 6	$5p\ ^3P_1-6d\ ^3P_0^\circ$	0
1848. 03	8+*H*	54111. 7	$5p\ ^3P_1-3351$	−2
1837. 58	6*R*	54419. 4		
1833. 08	4*h*	54553. 0		
1829. 28	3	54666. 3		
1828. 23	2	54697. 7	$5p\ ^3P_1-10s\ ^3P_1^\circ$	+1
1823. 00	120*Rs*	54854. 6		
1819. 31	25	54965. 9	$5p\ ^3P_1-6d\ ^1P_1^\circ$	−3
1815. 74	40*R*	55074. 0	$5p\ ^3P_0-6d\ ^3P_1^\circ$	0
1813. 04	30*r*	55156. 0	$5p\ ^3P_0-9s\ ^3P_1^\circ$	−2
1804. 93	10*r*	55403. 7	$5p\ ^3P_1-11s\ ^3P_1^\circ$	+2
1804. 60	80*Rl*	55413. 9		
1803. 16	8	55458. 1	$5p\ ^3P_1-8s\ ^3P_2^\circ$	−2
1795. 71	3	55688. 2		
1793. 35	10*HW*	55762.		
1790. 75	30*Rl*	55842. 5		
1789. 82	4*R*	55871. 5	$5p\ ^3P_1-12s\ ^3P_1^\circ$	−2
1787. 38	6	55947. 8	$5p\ ^3P_2-9s\ ^3P_2^\circ$	+5
1780. 46	5*R*	56165. 3		
1779. 12	*R*	56207. 6	$5p\ ^3P_1-13s\ ^3P_1^\circ$	+4
1777. 90	5	56246. 1		
1773. 40	20*rs*	56388. 9	$5p\ ^3P_0-10s\ ^3P_1^\circ$	−4
1764. 98	20*Rs*	56658. 0	$5p\ ^3P_0-6d\ ^1P_1^\circ$	0
1753. 3	10*H*	57035.		
1751. 46	15*Rl*	57095. 2	$5p\ ^3P_0-11s\ ^3P_1^\circ$	−1
1745. 75	3	57282. 0	$5p\ ^3P_0-8s\ ^1P_1^\circ$	−3
1737. 21	10*Rl*	57563. 6	$5p\ ^3P_0-12s\ ^3P_1^\circ$	+1
1733. 64	5*h*	57682. 1	$5p\ ^3P_1-9s\ ^3P_2^\circ$	−11
1729. 2	10*H*	57830.		
1727. 15	5*R*	57899. 0	$5p\ ^3P_0-13s\ ^3P_1^\circ$	0
1719. 87	*R*	58143. 9	$5p\ ^3P_0-14s\ ^3P_1^\circ$	0
1714. 54	*R*	58324. 7	$5p\ ^3P_0-15s\ ^3P_1^\circ$	0
1714. 12	*R*	58339. 0		
1697. 59	2*h*	58907. 0	$5p\ ^3P_1-10s\ ^3P_2^\circ$	0

All lines in table 1 were observed photographically except the first 37 (24738 to 12788 A), which are quoted (with corrections) from the radiometric observations of Randall and Wright [7]. These authors stated that the error in their measurements is roughly within 2 A, but the comparison of 20 lines (12535 to 9619 A) which both they and I measured shows that their scale is 1.8 A too large, so this amount was subtracted from each of their values.

Applying the combination principle as a test of the precision with which relative values of wavelengths are determined, the average residual, $\nu_{obs.}-\nu_{calc.}$, of the radiometric observations is 0.8 cm^{-1}, which corresponds approximately to 2 A, as estimated by Randall and Wright. The average residual for lines observed photographically is 0.09 cm^{-1}, which is equivalent to 0.1 A in the infrared at 11000 A, 0.01 A in the near ultraviolet at 3300 A, 0.004 A at 2000 A, and 0.002 A at 1700 A. It is no longer necessary to tolerate deviations of 10 or more wave numbers in discussing regularities among ultraviolet tin lines.

Relative intensities shown in column 2 of table 1 begin in the infrared with galvanometer deflections [in brackets] quoted from Randall and Wright [7], who took a deflection of 2,000 mm as average for the line at 11455 A and converted other lines to this scale by means of deflection ratios of adjacent lines. These quantitative relative intensities are in italics; the remainder are merely rough averages of the galvanometer deflections taken at different times.

The relative intensities based on visual estimates of the densities and widths of photographic images are subject to progressive errors near the infrared limit of photographic sensitivity; but elsewhere they should be fairly comparable, because variations are more or less averaged out by choosing exposures which give nearly uniform background throughout the spectrum. Besides intensities, column 2 contains some notes on the character of certain lines. When observed with care, the physical appearance of line images is a considerable aid in the analysis of spectral structure. Hazy lines almost invariably indicate that highly excited states are involved, while self-reversal is positive evidence that the line comes from the ground state or from some adjacent metastable state. Dissymmetries have been observed both among hazy and among reversed tin lines. The shading of hazy lines is usually toward longer waves, but occasionally this is reversed. The same is true of self-reversed lines; in some the outer edges shade strongly toward longer waves while others shade toward shorter waves. These effects are probably due to mutual perturbations of adjacent levels of opposite parity [22]. In addition, tin lines are widened by hyperfine structure [23], but the sources and spectrographs used in this investigation would hardly permit detection of this phenomenon. Symbols employed in table 1 for the description of line character are those adopted by the International Astronomical Union [24].

Eighty percent of the observed Sn I lines are classified, the analysis being almost complete for visible and near ultraviolet lines. In the infrared several strong lines (for example, 11277.66, 9850.52, and 9616.40 A) remain unclassified, and a half-dozen reversed lines in the extreme ultraviolet (1860.32, 1849.49, 1823.00, 1804.60, 1790.75, and 1780.46 A) have defied classification.

Summarizing the general features of the Sn I spectrum, attention is called to the paucity of visible lines, remarkable concentration of intensity in the near ultraviolet, and comparative richness in the infrared. One line of outstanding intensity, 4524.74 A, overwhelms all others in the visible spectrum and imparts a bluish color to the tin arc flame. The most intense line of the Sn I spectrum is undoubtedly 3262.34 A in the near ultraviolet, while 3801.02 and 3175.05 A vie for second place. Since the distribution of lines and intensity in any

atomic spectrum is a consequence of the atomic-energy states, it is now in order to discuss these aspects of tin atoms.

2. TERM STRUCTURE OF THE Sn I SPECTRUM

Tin has atomic number 50 and an electronic structure described as $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^2$. The observed optical spectrum can be (almost) completely accounted for by the two outermost valence electrons, which in various configurations give rise to theoretical spectral terms [25] shown in table 2.

TABLE 2.—*Theoretical terms of the* Sn I *spectrum*

Electron configurations	Spectral terms	
$5p^2$	$^3P_0$, $^3P_1$, $^3P_2$, $^1D_2$, $^1S_0$	
	Convergence limit $5p\ ^2P^0_{1/2}$ (Sn II)	Convergence limit $5p\ ^2P^0_{3/2}$ (Sn II)
$5p\ ns$	$^3P^0_0$, $^3P^0_1$	$^3P^0_2$, $^1P^0_1$
$5p\ np$	$^3D_1$, $^3D_2$, $^3P_0$, $^3P_1$	$^3D_3$, $^3P_2$, $^3S_1$, $^1D_2$, $^1P_1$, $^1S_0$
$5p\ nd$	$^3F^0_2$, $^3F^0_3$, $^3D^0_1$, $^3D^0_2$, $^3P^0_2$, $^3P^0_1$	$^3F^0_4$, $^3D^0_3$, $^3P^0_2$, $^1F^0_3$, $^1D^0_2$, $^1P^0_1$
$5p\ nf$	$^3G_3$, $^3G_4$, $^3F_2$, $^3F_3$, $^3D_1$, $^3D_2$	$^3G_5$, $^3F_4$, $^3D_3$, $^1G_4$, $^1F_3$, $^1D_2$

As stated in the introduction, the first significant regularities among arc spectrum lines of tin were discovered in 1894 by Kayser and Runge [3], who found 13 pairs of lines with the frequency difference 5187 cm^{-1} and 8 pairs separated 1736 cm^{-1}. In 1912, van Lohuizen [26] attempted to arrange tin lines in series, but the results were purely artificial. No further progress was made until 1918, when Zumstein [27] announced two more constant frequency differences, 1692 and 287 cm^{-1}, only the first of which is real. In 1924, McLennan, Young, and McLay [8] arranged most of the ultraviolet tin lines in a table of combinations with six levels of low energy separated successively by 1692, 1735, 288, 4897, and 8549 cm^{-1}. The fortuitous differences, 288 and 4897 cm^{-1}, were replaced by their sum, 5185 cm^{-1}, in a paper by H. Sponer [28], who criticized the work of McLennan, et al., on the grounds of large deviations among "constant" differences, numerous double classifications, and discrepancies among intensities and inner quantum numbers of terms proposed as series. In connection with his study of the absorption spectrum of tin vapor in the ultraviolet, Zumstein [9] compiled a table of 49 high levels with 5 low ones, and Sur [29] promptly conjectured the first quantum interpretation of some of these. The identification of five lowest levels with $^3P_0$, $^3P_1$, $^3P_2$, $^1D_2$, $^1S_0$ characteristic of a p^2 configuration was obvious, but the other designations were more or less arbitrary and incorrect. The first real information about the nature of these levels resulted from the Zeeman-effect investigations of Back [10] and of Green and Loring [11], which definitely fixed the quantum numbers of the $5p^2$, $5p5d$, $5p5s$, and a few more levels. Another attempt at quantum description of tin levels and arrangement in series was made in 1929 by Williams and Charola [30], but their results are largely vitiated by the use of unreliable data

already cited which tolerates deviations up to 12 cm^{-1} in relative values of energy levels. An important contribution was made in 1931 by Randall and Wright [7], who observed new lines in the infrared and established some levels of the $5p6p$, $5p4f$, and $5p5f$ configurations.

The present investigation, being based on a more complete and accurate description of the Sn I spectrum, has unmasked numerous errors in all preceeding classifications of Sn I lines. Many levels parading in the literature as real are not confirmed, but are replaced by others resting for the most part on combinations which cannot be regarded as fortuitous. In some cases new combinations have corrected the j values of previously known levels.

Besides the levels belonging to $5p^2$, levels from $5pns$ have been traced from $n=6$ to $n=15$, the levels (except $^3F_4$) from $5p5d$ and $5p6d$ (and fragments of $5p7d$ and $5p8d$) have been established, levels from $5p6p$ and $5p7p$ have been revised and completed, while additional levels from $5p4f$ and $5p5f$ have been found.

The $5p-ns$ combinations are displayed in table 3, so that the series may be critically examined. The only extended series found, or expected, in the Sn I spectrum are collected here, and will be discussed in more detail below.

TABLE 3.—*5p-ns combinations of* Sn I

Term symbol	Value	$5p^2\ ^3P_0$	$5p^2\ ^3P_1$	$5p^2\ ^3P_2$	$5p^2\ ^1D_2$	$5p^2\ ^1S_0$
Value		59155.0	57463.2	55727.3	50542.0	41992.4
$5p(^2P^0_{1/2})6s\ ^3P^0_0$	*24514.2*		32948.92(900*R*)			
$^3P^0_1$	*24240.8*	34914.22(600*R*)	33222.48(700*R*)	31486.53(2000*R*)	26301.26(2000*R*)	17751.69(500)
$5p(^2P^0_{3/2})6s\ ^3P^0_2$	*20526.2*		36937.02(1000*R*)	35201.1(700*R*)	30015.84(500*r*)	
$^1P^0_1$	*19897.9*	39257.05(400*r*)	37565.27(200*R*)	35829.4(4)	30644.04(2500*R*)	22094.52(1000)
$5p(^2P^0_{3/2})7s\ ^3P^0_2$	*10938.8*		46524.36(40R)			
$^3P^0_1$	*10952.9*	48222.0(100*r*)	46530.26(15*r*)	44794.43(80*R*)	39609.08(90*r*)	31059.44(40)
$5p(^2P^0_{3/2})7s\ ^3P^0_2$	*6739.3*		50723.9(30)	48987.95(50)	43802.72(20)	
$^1P^0_1$	*6448.2*	52706.8(20)	51014.9(15)	49279.20(5)	44093.87(30*r*)	35544.0(60)
$5p(^2P^0_{3/2})8s\ ^3P^0_2$	*6151.9*		51311.3(2)			
$^3P^0_1$	*6154.4*	53020.9(80*r*)	51328.8(8)	49592.89(30)	44407.59(60*r*)	35858.0(60)
$5p(^2P^0_{1/2})8s\ ^3P^0_2$	*2004.9*		55458.1(8)	53722.4(20)	48537.24(5)	
$^1P^0_1$	*1872.7*	57282.0(3)			48669.10(50*h*)	40119.8(10*h*)
$5p(^2P^0_{3/2})9s\ ^3P^0_2$						
$^3P^0_1$	*3998.8*	55156.0(30*r*)	53464.5(1)	51728.5(25)	46543.09(6)	37993.0(7*Hl*)
$5p(^2P^0_{1/2})9s\ ^3P^0_2$	*−220.*		57682.1(5)	55947.8(6)	50761.9(1)	
$^1P^0_1$						
$5p(^2P^0_{3/2})10s\ ^3P^0_2$						
$^3P^0_1$	*2765.7*	56388.9(20*r*)	54697.7(2)	52961.6(3)	47776.25(3)	39226.5(5*hl*)
$5p(^2P^0_{1/2})10s\ ^3P^0_2$	*−1445.8*		58907.0(2)			
$^1P^0_1$						
$5p(^2P^0_{3/2})11s\ ^3P^0_2$						
$^3P^0_1$	*2059.7*	57095.2(15*R*)	55403.7(10*r*)			
$5p(^2P^0_{1/2})11s\ ^3P^0_2$						
$^1P^0_1$						
$5p(^2P^0_{3/2})12s\ ^3P^0_2$						
$^3P^0_1$	*1591.5*	57563.6(10*R*)	55871.5(4*R*)			
$5p(^2P^0_{1/2})12s\ ^3P^0_2$						
$^1P^0_1$						
$5p(^2P^0_{3/2})13s\ ^3P^0_2$						
$^3P^0_1$	*1256.0*	57899.0(*R*)	56207.6(*R*)			
$5p(^2P^0_{1/2})13s\ ^3P^0_2$						
$^1P^0_1$						
$5p(^2P^0_{3/2})14s\ ^3P^0_2$						
$^3P^0_1$	*1011.*	58143.9(*R*)				
$5p(^2P^0_{1/2})14s\ ^3P^0_2$						
$^1P^0_1$						
$5p(^2P^0_{3/2})15s\ ^3P^0_2$						
$^3P^0_1$	*880.*	58324.7(*R*)				

The $6s-np$ combinations are shown in table 4. Randall and Wright [7] gave ten $6p$ and four $7p$ levels; my analysis confirms eight of the former (except j values for 11349 and 10965) and three of the latter (except j value of 7984). Whereas they adopted $\nu=8863$ as $5p6s\ {}^1P_1^\circ-5p6p\ {}^1S_0$, I have substituted $\nu=7679$, because it was the outstanding unclassified strong line. Neither assumption is checked by any other combination. No evidence of levels from the $5p8p$ configuration has been found.

TABLE 4.—*6s—np combinations of* Sn I

Term symbol	Value	$5p6s\ {}^3P_0^\circ$ *24514.2*	$5p6s\ {}^3P_1^\circ$ *24240.8*	$5p6s\ {}^3P_2^\circ$ *20526.2*	$5p6s\ {}^1P_1^\circ$ *19897.9*
$5p(^3P_{0,1}^\circ)6p\ {}^3D_1$	16812.7	7701.0[*1870*]	7427.3[*3780*]		
$^3D_2$	15916.3		8324.47[*480*]	4610.0[80]	
$^3P_1$	15786.5	8727.74[*2000*]	8454.22[*960*]		4109.5[40]
$^3P_0$	15715.0		8515.72[*2580*]		
$5p(^3P_{1,2}^\circ)6p\ {}^1P_1$	12551.6	11962.68(80)	11689.14(400)	7974.52[425]	7346.5[*1440*]
$^1S_0$	12218.7?				7679.2[*1870*]
$^3D_3$	12148.2			8377.84[*2540*]	
$^3P_2$	11919.8		12320.86(200)	8606.27[*2090*]	7978.11[425]
$^3S_1$	11349.3	13164.93(2)	12891.41(100)	9176.85[*540*]	8548.72[*250*]
$^1D_2$	10965.3		13275.3(1)	9560.84[*250*]	8932.63[*700*]
$5p(^3P_{0,1}^\circ)7p\ {}^3D_1$	8399.2	16115.12(20*h*)	15841.53(100*h*)	12127.0(1*h*)	11498.86(5*h*)
$^3D_2$	7984.2		16256.44(400*hs*)	12542.00(8*h*)	11913.82(20*h*)
$^3P_1$	8041.7	16472.63(250*hs*)	16199.04(150*h*)	12484.5(1*h*)	11856.13(5*h*)
$^3P_0$	7780.2		16460.53(100*h*)		12117.84(8*h*)
$5p(^3P_{1,2}^\circ)7p\ {}^1P_1$	4165.0	20349.24(3*h*)	20075.83(20*h*)	16361.08(4*h*)	15732.91(40*h*)
$^1S_0$	6889.7		17351.01(10*h*)		13008.28(30*h*)
$^3D_3$	4015.1			16511.10(200*hl*)	
$^3P_2$	3968.1		20272.70(10*h*)	16558.02(150*hl*)	15929.95(5*h*)
$^3S_1$	3781.2		20459.44(2*h*)	16744.95(100*h*)	16116.76(3*h*)
$^1D_2$	3654.4			16871.72(50*hl*)	16243.52(200*h*)

All $5p-nd$ combinations are presented in table 5. The $6d$ levels were tentatively selected by comparing relative positions and combining properties with those of the well-established $5d$ levels. There are, however, some intensity anomalies which may be due to perturbations of other levels. Because of almost complete overlapping of $6d$, $7d$, and $8d$ configurations, and the fragmentary character of the higher terms, it seems presumptuous to attempt grouping these higher levels into terms and series.

Table 5 also shows combinations of two superfluous levels at *19529* and *11919* cm^{-1}, which possibly belong to the $5s5p^3$ configuration.

Unfortunately it is still impossible to establish all expected levels from the $5pnf$ configurations, principally on account of insufficient infrared data. Their strongest combinations range in wave number from 2000 to 13000 cm^{-1}, part of which range has never been explored, and faint lines are unrecorded in most of the remainder. Randall and Wright [7] reported no galvanometer deflections less than 30 mm. Inability at the present time to complete the full sets of levels due to $5pnf$ curbs the possibility of establishing $5p5d\ {}^3F_4$; its j value is too large to permit combination with any $5p^2$ levels. Randall and Wright [7] reported some $ns-nf$ combinations, but no evidence for such combinations is found among my data.

TABLE 5.—*5p—nd combinations of* Sn I

Term symbol	Value	$5p^2\ ^3P_0$ 59155.0	$5p^2\ ^3P_1$ 57463.2	$5p^2\ ^3P_2$ 55727.3	$5p^2\ ^1D_2$ 50542.0	$5p^2\ ^1S_0$ 41992.4
$5p(^3P_{0\frac{1}{2}})5d\ ^3D_1$	*15472.0*		41991.3(60)	40255.35(300*r*)	35069.8(200*r*)	
$^3F_2$	*15010.4*		42452.78(1000*R*)	40716.97(60)	35531.53(80)	
$^3D_2$	*14646.2*	44508.80(400*R*)	42817.1(300*R*)	41081.16(15)	35895.69(80)	27346.20(250)
$^3F_3$	*14578.9*			41148.44(1000*R*)	35963.09(150)	
$5p(^3P_{1\frac{1}{2}})5d\ ^1D_2$	*13009.5*		45454.01(300*R*)	43717.97(200*R*)	38532.69(200*R*)	
$^3D_1$	*11667.0*			44060.31(400*R*)	38875.02(500*R*)	
$^3P_2$	*10485.4*		46977.68(7)	45241.88(400*R*)	40056.78(200*r*)	
$^3P_1$	*10173.0*	48982.07(15)	47290.2(100*R*)	45554.31(150*R*)	40369.08(20)	31819.34(60)
$^3P_0$	*9667.8*		47795.44(30*r*)			
$^1F_3$	*9261.2*			46466.0(20*R*)	41280.81(800*R*)	
$^1P_1$	*9029.1*	50125.9(20)	48434.11(20)	46698.17(25*r*)	41513.0(100)	32963.21(200*h*)
$5p(^3P_{1\frac{1}{2}})6d\ ^3D_2$	*8144.5*		49318.64(30)	47582.71(100)	42397.71(20*h*)	
$^3F_3$	*7994.8*		49468.51(10)	47732.32(40)		
$^3D_1$	*7679.9*	51475.1(20)	49783.42(25)	48047.27(25)	42861.95(6*h*)	34312.45(200*h*)
$^3F_2$	*7490.5*			48326.67(80*r*)	43141.7(600*R*)	
$5p(^3P_{1\frac{1}{2}})6d\ ^1D_2$	*5858.9*		53604.3(20)	51868.6(15)	46682.91(20)	
$^3D_3$	*5415.3*			52312.0(40)	47126.74(50*h*)	
$^3P_2$	*4501.6*		52961.6(3)	51225.6(150*r*)	46040.4(80*r*)	
$^3P_1$	*4081.0*	55074.0(40*R*)	53382.1(15)			37911.5(50*H*)
$^3P_0$	*3872.6*		54090.6(30*R*)			
$^1F_3$	*2856.2*			52871.0(100*r*)	47685.8(200*r*)	
$^1P_1$	*2497.0*	56658.0(20*R*)	54965.9(25)	53230.3(5)		39495.6(80*H*)
$5s5p^3\ ?$ 2	*16589.5*		37933.67(?)	36197.9(20)	31012.57(10)	
3	*11919.8*			43807.5(2)	38622.20(7)	
$5p(^3P_{0\frac{1}{2}})7d\ ^3D_1$	*5562.8*	53592.1(30*r*)	51900.4(20)	50164.6(3)	44979.23(6*h*)	36429.9(2*h*)
$^3F_2$	*5523.6*		51939.8(80*r*)	50203.7(15)	45018.35(10*h*)	
$^3F_3$	*5329.0*			50398.2(80)	45213.2(40*r*)	
5p 7d and *5p 8d*	*4943.3*		52519.9(2)	50784.0(4)		
	4442.2			51285.2(1)	46099.84(2)	
	4324.1			51403.3(3)	46217.90(5)	
	3407.6		53995.6(30)	52259.6(20)	47074.50(7*h*)	
	3351.3		54111.7(8)		47190.9(10*h*)	
	2911.3				47630.6(3)	39081.2(40*H*)
	2610.2			53117.0(30*h*)	47932.0(5)	
	2315.5			53411.9(10*h*)	48226.4(100*h*)	

3. SPECTRAL SERIES AND IONIZATION POTENTIAL

Since law-abiding spectral series are always of special interest and importance for determinations of spectroscopic ionization potentials and for tracing the convergence of term sequences in one spectrum to limits in the next, we shall now return to the $5p—ns$ combinations. Any s electron reacting with $5p$ gives rise to four energy levels, $^1P^\circ$, $^3P^\circ_0$, $^3P^\circ_1$, $^3P^\circ_2$, which with increasing n converge toward the ground state of the ion represented by $5p\ ^2P^\circ_{0\frac{1}{2},1\frac{1}{2}}$. Furthermore, as shown in table 2, two of the levels ($^3P_0$ and $^3P_1$) end on $^2P^\circ_{0\frac{1}{2}}$, while the remaining two ($^1P_1$ and $^3P_2$) end on $^2P^\circ_{1\frac{1}{2}}$. The ^2P term describing the normal state of a tin ion has a level separation of 4252 cm^{-1}, according to Green and Loring [11] or Narayan and Rao [31], and this large interval divides the levels belonging to any configuration with a running electron into two widely separated groups.

As a general rule, the most prominent and longest series of lines or terms in any spectrum is the series which involves the normal state of the atom (or ion) and produces lines which are easily self-reversed, or observed in pure absorption. This rule is obeyed by the Sn I spectrum, in which I have succeeded in tracing the sequence of $ns\ ^3P_1$ levels for 10 values of n from $n=6$ to $n=15$. The tail end of this series was observed only in absorption, the last three lines appearing as reversals in the continuous background on the spectrograms.

Although the $ns\,^3P_2$ levels have larger j values (usually accompanied by stronger combinations), they cannot combine with the ground level, $^3P_0$, because $\Delta j=2$, and combinations with the first metastable state, $^3P_1$, cannot be followed beyond five members, that is, from $n=6$ to $n=10$. The $ns\,^3P_0$ levels can combine only with $^3P_1$, and the fourth line could hardly be expected when the intensities of the first three are observed to be in the ratio 900, 40, 2. A rapid intensity decrement also limits the intersystem series $5p\,^3P_0-ns\,^1P_1$ to three lines with relative intensities 400, 20, 3.

A Ritz formula of the type

$$\nu=L-R/\left(n+a+\frac{b}{n^2}\right)^2,$$

in which $R_{Sn}=109737.0$, has been calculated to represent each of the above-mentioned series. The series $5p\,^3P_0-ns\,^3P_1^\circ$ is satisfactorily reproduced by the formula

$$\nu=59160-109737/\left(n-3.64395-\frac{8.22715}{n^2}\right)^2, n=6, 7, 8, \ldots$$

The "observed minus calculated" wave numbers for 10 successive lines are $-2,-142,+1,-29,+17,+1,-3,+6,+15,+20$. In other words, the average error in wavelength representation of nine lines is ± 0.4 A, and the calculated position of the second line is 6.2 A too short. This raises a question concerning the identification of two levels, *10932* and *10173*, designated $7s\,^3P_1^\circ$ and $5d\,^3P_1^\circ$, respectively, by Green and Loring [11], but the reverse by Back [10]. Both attached question marks to their designations of the latter level, but present evidence favors the former interpretation. If the latter were correct, the calculated position of the second series line would be 27 A too short and there would be an additional intensity anomaly.

The series $5p\,^3P_1-ns\,^3P_2^\circ$ is represented by the formula

$$\nu=61703-109737/\left(n-3.68077-\frac{7.72844}{n^2}\right)^2, n=6, 7, 8, \ldots$$

with the following "observed minus calculated" wave numbers for five successive lines: $+10, \pm 0, -19, \pm 0, +20$. This series converges toward $^2P^\circ_{1\frac{1}{2}}$ of Sn II; and since $5p\,^3P_1$ is removed 1692 cm^{-1} from $5p\,^3P_0$, this amount must be added to the limit to obtain the energy difference $5p^2.{}^3P_0$ (Sn I) $-5p.{}^2P^\circ_{1\frac{1}{2}}$ (Sn II) $=61703+1692=63395$ cm^{-1}.

The Ritz formula

$$\nu=57640-109737/\left(n-3.76466-\frac{4.57780}{n^2}\right)^2, n=6, 7, 8,$$

fits the three-line series $5p\,^3P_1-ns\,^3P_0^\circ$ perfectly. Since $5p\,^3P_1$ is 1692 cm^{-1} from $5p\,^3P_0$, an absolute value of $57640+1692=59332$ is indicated for the latter.

Likewise, the Ritz formula

$$\nu=63286-109737/\left(n-3.54774-\frac{11.35288}{n^2}\right)^2, n=6, 7, 8,$$

represents without error the three-line series $5p\,^3P_0-ns\,^1P_1^\circ$. The limit, 63286, is a measure of the energy difference $5p^2.{}^3P_0$

(Sn I)$-5p\cdot{}^2P^\circ_{1½}$(Sn II), to be compared with 63395 obtained from the five-line series, $5p\,{}^3P_1-ns\,{}^3P^\circ_2$. Regarding the latter twice as reliable as the former, we obtain a weighted mean of 63360; and subtracting the doublet separation of the Sn II ground state, we obtain 63360$-$4252$=$59107 cm^{-1} as the absolute value of $5p\,{}^3P_0$.

By assigning three times as much weight to the 10-line series, $5p\,{}^3P_0-ns\,{}^3P^\circ_1$, as to the three-line series, $5p\,{}^3P_1-ns\,{}^3P^\circ_0$, we obtain 59203 cm^{-1} as the absolute value of $5p\,{}^3P_0$. Finally, the average of 59107 and 59203 is 59155 cm^{-1}, which is the value I have adopted as the basis for all Sn I terms. This is almost identical with 59160 given by the 10-term series. After this value, 59155, was adopted, I noticed that in 1924 McLennan, et al. [8], by assuming that the frequencies 54098, 54428, 54672, and 54852 formed a Rydberg series with values of m equal to 8, 9, 10, and 11 arrived at a value of 59158 for this constant. This must be regarded as a most remarkable coincidence, because the assumed series is entirely fictitious, none of the levels being confirmed.

The only subsequent attempts to derive the absolute value of Sn I terms were made by Green and Loring [11] in 1927 and by Randall and Wright [7] in 1931. The former correctly classified the first three lines of the series $5p^3P_0-ns\ {}^3P^\circ_1$, and the value of $5p^3P_0$ was computed approximately as 59690 cm^{-1}. Randall and Wright assumed that two unidentified levels (6891 and 4387 cm^{-1} in my list) represented $5p\ ({}^2P^\circ_{0½})\ 4f$ and $5p\ ({}^2P^\circ_{0½})\ 5f$ terms in a Rydberg series and thus obtained 59192 cm^{-1} for the absolute value of the lowest level of Sn I.

The value 59155 for $5p^2.{}^3P_0$ (Sn I) corresponds to an ionization potential of $1.2336\times10^{-4}\times59155=7.297$ volts. If the series electron is driven to the higher level of the Sn^+ ion, the potential necessary for ionization will be $1.2336\times10^{-4}\times(59155+4252)=7.822$ volts.

An impression of the reliability of the limits derived from the various ns sequences may perhaps be obtained from a comparison of 59203 and 63360. Since the former is given by two series converging to ${}^2P^\circ_{0½}$(Sn II) and the latter by two series converging to ${}^2P^\circ_{1½}$ (Sn II), the difference, 4157 cm^{-1}, is a measure of the level separation in the ${}^2P$ term representing the normal state of ionized tin atoms. The true value of this separation is 4252 cm^{-1} as stated before [11, 31].

All the Sn I levels and terms that I have been able to establish and interpret with reasonable certainty are exhibited in table 6. Rather than arrange the levels in strict order of magnitude and thereby mix up a variety of terms and configurations, I have preferred to group the levels primarily under configurations and secondarily in order of energy. So far as possible like levels from similar configurations are repeated in the same order so that they may be easily compared. Intervals between levels of triplet terms are shown in column 4. The "level separation" opposite any particular level expresses the distance in cm^{-1} from that level to the one with unit greater j value. It will be noticed that many of these level separations are of the order of 4000 cm^{-1}, suggestive of the two ionic states toward which all Sn I series converge. Indeed, it is the 4252 cm^{-1} wide doublet of Sn II which divides into two groups all Sn I levels belonging to any configuration with a running electron. Because this convergence interval is larger than any interval between successive terms (beyond the second), it results in a confusing inter-

lacing or overlapping of terms probably entailing perturbations of intervals, intensities, and magnetic splitting factors, thus destroying all simple criteria of term designations. When there is such promiscuity between coupled electrons, the begotten terms will have difficulty in recognizing their parents. In the presence of such superposition, although numerous transitions between levels are theoretically possible, many of the resulting lines are probably in the still unexplored infrared, and the levels themselves cannot be established except through the lines associated with them.

TABLE 6.—*Levels and terms of* Sn I

Electron configuration	Term symbol	Term value cm^{-1}	Level separation
$5p^3$	$^3P_0$	59155. 0	1691. 8
	$^3P_1$	57463. 2	1735. 9
	$^3P_2$	55727. 3	
	$^1D_2$	50542. 0	
	$^1S_0$	41992. 4	
$5p(^2P^\circ_{0\frac{1}{2}})6s$	$^3P^\circ_0$	*24514. 2*	273. 4
	$^3P^\circ_1$	*24240. 8*	3714. 6
$5p(^2P^\circ_{1\frac{1}{2}})6s$	$^3P^\circ_2$	*20526. 2*	
	$^1P^\circ_1$	*19897. 9*	
$5p(^2P^\circ_{0\frac{1}{2}})6p$	$^3D_1$	16812. 7	896. 4
	$^3D_2$	15916. 3	3768. 1
	$^3P_1$	15786. 5	3866. 7
	$^3P_0$	15725. 0	−61. 5
$5p(^2P^\circ_{1\frac{1}{2}})6p$	$^1P_1$	12551. 6	
	$^1S_0$	12218. 7?	
	$^3D_3$	12148. 2	
	$^3P_2$	11919. 8	
	$^3S_1$	11349. 3	
	$^1D_2$	10965. 3	
$5p(^2P^\circ_{0\frac{1}{2}})5d$	$^3D^\circ_2$	*15472. 0*	3805. 0
	$^3F^\circ_2$	*15010. 4*	431. 5
	$^3D^\circ_1$	*14646. 2*	−825. 8
	$^3F^\circ_3$	*14578. 9*	
$5p(^2P^\circ_{1\frac{1}{2}})5d$	$^1D^\circ_2$	*12009. 3*	
	$^3D^\circ_3$	*11667. 0*	
	$^3P^\circ_2$	*10485. 4*	
	$^3P^\circ_1$	*10173. 0*	−312. 4
	$^3P^\circ_0$	*9667. 8*	−495. 2
	$^1F^\circ_3$	*9261. 2*	
	$^1P^\circ_1$	*9029. 1*	
$5p(^2P^\circ_{0\frac{1}{2}})7s$	$^3P^\circ_0$	*10938. 8*	5. 9
	$^3P^\circ_1$	*10932. 9*	4193. 6
$5p(^2P^\circ_{1\frac{1}{2}})7s$	$^3P^\circ_2$	*6739. 3*	
	$^1P^\circ_1$	*6448. 2*	
$5p(^2P^\circ_{0\frac{1}{2}})7p$	$^3D_1$	8399. 2	415. 0
	$^3D_2$	7984. 2	3969. 1
	$^3P_1$	8041. 7	4073. 6
	$^3P_0$	7780. 2	−619. 0
$5p(^2P^\circ_{1\frac{1}{2}})7p$	$^1P_1$	4165. 0	
	$^1S_0$	6889. 7	
	$^3D_3$	4015. 1	
	$^3P_2$	3968. 1	
	$^3S_1$	3781. 2	
	$^1D_2$	3654. 4	
$5p(^2P^\circ_{0\frac{1}{2}})6d$	$^3D^\circ_2$	*8144. 5*	4729. 2
	$^3F^\circ_2$	*7994. 8*	594. 3
	$^3D^\circ_1$	*7679. 9*	−464. 6
	$^3F^\circ_3$	*7400. 5*	

TABLE 6.—*Levels and terms of* Sn I—Continued

Electron configuration	Term symbol	Term value cm^{-1}	Level separation
$5p(^2P^1_{1/2})6d$	$^1D^2_2$	*3858. 9*	
	$^3D^2_3$	*3415. 3*	
	$^3P^2_2$	*4501. 6*	
	$^3P^2_1$	*4081. 0*	−420. 6
	$^3P^2_0$	*3372. 6*?	−708. 4
	$^1F^2_3$	*2856. 2*	
	$^1P^2_1$	*2497. 0*	
$5p(^2P^2_{3/2})4f$	1, 2, 3	6906. 0	
	2	6891. 2	
$5p(^2P^2_{3/2})5f$	2, 3	4392. 4	
	1, 2, 3	4387. 3	
	2	4383. 2	
$5p(^2P^1_{1/2})4f$	2, 3	2759. 0	
	4	2754. 3	
	2	2668. 5	
	1	2666. 5	
	4	2605. 0	
	2	2522. 1	
$5p(^2P^1_{1/2})5f$	4	108. 4	
5s $5p^2$?	2	*19529. 5*	
	3	*11919. 8*	
$5p(^2P^2_{3/2})7d$	$^3D^2_1$	*5562. 8*	
	$^3F^2_2$	*5523. 6*	194. 6
	$^3F^2_3$	*5329. 0*	
5p 7d	2	*4943. 3*	
and 5p 8d	3	*4442. 2*	
	3	*4324. 1*	
	2	*3467. 6*	
	2	*3351. 3*	
	1	*2911. 3*	
	3	*2610. 2*	
	3	*2315. 5*	
$5p(^2P^2_{3/2})8s$	$^3P^2_0$	*6151. 9*	17. 5
	$^3P^2_1$	*6134. 4*	4129. 5
$5p(^2P^1_{1/2})8s$	$^3P^2_2$	*2004. 9*	
	$^1P^2_1$	*1872. 7*	
$5p(^2P^2_{3/2})9s$	$^3P^2_1$	*3998. 8*	4219.
$5p(^2P^1_{1/2})9s$	$^3P^2_2$	*−220. 0*	
$5p(^2P^2_{3/2})10s$	$^3P^2_1$	*2765. 7*	4209. 5
$5p(^2P^1_{1/2})10s$	$^3P^2_2$	*−1443. 8*	
$5p(^2P^2_{3/2})11s$	$^3P^2_1$	*2059. 7*	
$5p(^2P^2_{3/2})12s$	$^3P^2_1$	*1591. 5*	
$5p(^2P^2_{3/2})13s$	$^3P^2_1$	*1256. 0*	
$5p(^2P^2_{3/2})14s$	$^3P^2_1$	*1011. 1*	
$5p(^2P^2_{3/2})15s$	$^3P^2_1$	*830. 3*	

Another consequence of the wide doublet to which Sn I terms converge is that high terms going to the upper limit may exceed the lower ionization energy and become negative. Several negative terms are listed near the end of table 6. It was shown above that a potential of 7.297 volts measures the energy required to move a valence electron from its normal state in a neutral Sn atom to the lowest energy state of the Sn^+ ion, and that ionization to the higher (metastable) ionic state increases the potential to 7.822 volts. The former value, 7.297 volts, expresses the *principal ionization potential* of tin.

IV. REFERENCES

[1] W. F. Meggers, J. Opt. Soc. Am. **29,** 258 (1939).
[2] H. Kayser, Handbuch der Spectroscopie **6,** 509 (1912).
[3] H. Kayser and C. Runge, Wiedem. Ann. **52,** 93 (1894).
[4] R. Arnolds, Z. wiss. Phot. **13,** 313 (1914).
[5] F. M. Walters, Jr., BS Sci. Pap. **17,** 174 (1921) S411.
[6] H. M. Randall, Astrophys. J. **34,** 1 (1911).
[7] H. M. Randall and N. Wright, Phys. Rev. **38,** 457 (1931).
[8] J. C. McLennan, J. F. T. Young, and A. B. McLay, Trans. Roy. Soc. Can. **18,** 57 (1924).
[9] R. V. Zumstein, Phys. Rev. **27,** 150 (1926).
[10] E. Back, Z. Physik **43,** 309 (1927).
[11] J. B. Green and R. A. Loring, Phys. Rev. **30,** 574 (1927).
[12] A. G. Shenstone, Phil. Trans. Roy. Soc. (London) [A] **237,** 453 (1938).
[13] W. F. Meggers and K. Burns, BS Sci. Pap. **18,** 185 (1922) S441.
[14] R. W. Wood, Nature, **140,** 723 (1937).
[15] Eastman Kodak Co., Photographic Plates for Use in Spectroscopy and Astronomy (1935).
[16] Proc. Sixth Summer Conference on Spectroscopy, p. 114 (John Wiley & Sons, New York, N. Y., 1939).
[17] K. Burns and F. M. Walters, Jr., Pub. Allegheny Obs. **6,** 159 (1929); **8,** 39 (1931); **8,** 27 (1931).
[18] J. C. Boyce and H. A. Robinson, J. Opt. Soc. Am. **26,** 133 (1936).
[19] W. F. Meggers, J. Research NBS **14,** 33 (1935) RP755; W. F. Meggers and C. J. Humphreys, J. Research NBS **18,** 543 (1937) RP992.
[20] H. Kayser, Tabelle der Schwingungszahlen (Julius Springer, Berlin, 1927).
[21] W. F. Meggers and C. G. Peters, Bul. BS **14,** 697 (1918) S327.
[22] T. L. deBruin, C. J. Humphreys and W. F. Meggers, BS J. Research **11,** 417 (1933) RP599.
[23] H. Schüler and H. Westmeyer, Naturwissenschaften **21,** 660 (1933); S. Tolansky, Proc. Roy. Soc. (London) [A] **144,** 574 (1934).
[24] Trans. Int. Astron. Union **6,** 100 (1938).
[25] F. Hund, Linienspektren und Periodisches System der Elemente (Julius Springer, Berlin, 1927).
[26] J. van Lohuizen, Z. wiss. Phot. **11,** 397 (1912).
[27] R. V. Zumstein, Trans. Roy. Soc. Can. **12,** 59 (1918).
[28] H. Sponer, Z. Physik **32,** 19 (1925).
[29] N. K. Sur, Z. Physik **41,** 791 (1927).
[30] A. T. Williams and F. Charola, J. phys. **9,** 377 (1929).
[31] A. L. Narayan and K. R. Rao, Z. Physik **45,** 350 (1927).

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REACTION OF BROMINE WITH FURFURAL AND RELATED COMPOUNDS

By Elizabeth E. Hughes and S. F. Acree

ABSTRACT

The mechanism of the reaction of bromine in aqueous solution with furfural and with two related compounds is discussed.

The bromine present and the acidity of the solutions were each determined after various periods of time at 0° C, to obtain a measure of the bromine consumed, the amount of acid used in liberation of bromine, and the hydrobromic acid generated during the reaction. The product of the reaction of molar proportions of bromine and furfural was precipitated with phenylhydrazine and analyzed. Its composition and the analytical data indicate that when molar proportions of bromine and furfural react, the bromine is changed to bromide ions, 2 equivalents of hydrogen ions are formed from the water, and 2 equivalents of hydroxyl ions or oxygen combine with the furfural.

During a study of the quantitative determination of furfural with bromine, some phases of the mechanism of the reaction were also investigated. The determination depends upon the oxidation of furfural by bromine liberated from a solution of bromate and bromide.

Work by Hill and Sanger [1],[1] Gilman and Wright [2], and others indicates that in some organic solvents bromine reacts with some furane derivatives by preliminary addition at a double bond, to form a dibromo compound (reactions I and II), which may then be made to lose hydrobromic acid and yield a bromofurane (reaction II). For some unsaturated compounds in water or alcohols, however, it has been shown by Conant and Jackson [3], Dimroth, Schultze, and Heinze [4], Bartlett and Tarbell [5], and others that one hydroxyl or alkoxyl group and one bromine atom may add at a double bond in preference to two atoms of bromine (reaction III). The presumed course of the reaction is indicated as follows:

[1] Figures in brackets indicate the literature references given at the end of this article.

I. $Br_2 + -CH=CH- \longrightarrow -CH^+-CH^+- + Br^- Br^- \longrightarrow -CHBr-CHBr-$
II. $Br_2 +$ HC—CH / HC C—CHO \ O $\longrightarrow$ BrHC—CH / BrHC C—CHO \ O (4- or 5-bromo) $\xrightarrow{(-HBr)}$ HC—CH / BrC C—CHO \ O
III. $Br_2 + [H^+ OH^-] + xBr^- +$ HC—CH / HC C—CHO \ O $\longrightarrow HBr + xBr^- +$ HOHC—CH / BrHC C—CHO \ O $\xrightarrow{(-H_2O)}$ HC—CH / BrC C—CHO \ O $\xrightarrow{(-HBr)}$ HOC—CH / HC C—CHO \ O (4- or 5- enol) $\longleftrightarrow$ O= C—CH / H_2C C—CHO \ O (4- or 5-keto)
IV. $Br_2 + 2[H^+ OH^-] + xBr^- +$ HC—CH / HC C—CHO \ O $\longrightarrow 2\,HBr + xBr^- +$ HOHC—CH / HOHC C—CHO \ O $\xrightarrow{(-H_2O)}$ HOC—CH / HC C—CHO \ O
V. $Br_2 + 2[H^+ OH^-] + xBr^- +$ HC—CH / HC C—CHO \ O $\longrightarrow 2\,HBr + xBr^- + H_2O +$ HC—CH / HC C—COOH \ O

The course of the reaction is determined by the dielectric constant of the solvent through its influence on the electronic exchanges which take place. There exists also the possibility of the addition of two hydroxyl groups at a double bond (reaction IV), or of oxidation of the aldehyde group to carboxyl (reaction V). Additions of OH^- and Br^- at the 4,5 positions are assumed in the above reactions merely for convenient representation. The structure was not determined, and substitution or addition may occur at other positions.

Data on the change in acidity during the reactions and information on the end products formed may differentiate between the various possibilities. In reaction II and in III, 1 equivalent of hydrobromic acid is formed; in IV or a sequence of III and IV as shown, 2 equivalents of hydrobromic acid are formed; and in V, 2 equivalents of hydrobromic acid and one carboxyl group, or 3 equivalents of acid, are formed. In this work there was no attempt to distinguish between the reactions of the 2,3 and 4,5 double bonds of furfural compounds or of their conjugated 2,5- systems.

In the experiments bromine was liberated at 0° C from 25 ml of a solution of 0.1 *N* potassium bromate-bromide by an equivalent amount of hydrobromic acid in the presence of molar equivalents of the reducing substance. As 2 equivalents of hydrobromic acid are slowly used up to liberate 1 mole of bromine according to the equation

$$KBrO_3 + 6H^+ + 6Br^- \rightarrow KBr + 3H_2O + 3Br_2,$$

individual experiments were performed for different periods of time from 1 hour through several hours or days. Under these conditions, when 1 mole of bromine reacts with 1 mole of furfural, methylfurfural, or furoic acid there is no bromine color apparent at any time. This indicates that the bromine is consumed as soon as it is liberated.

In each experiment the acid was first titrated with 0.1 *N* solution of sodium hydroxide, using phenolphthalein as the indicator, and the remaining bromate was then determined iodometrically after the addition of potassium iodide and concentrated hydrochloric acid. With known amounts of acid and of available bromine present at the beginning of the reaction, one may calculate the bromine consumed, which is liberated by an equivalent amount of acid, and the amount of acid regenerated. The figures in tables 1 and 3 show that in the cases of furfural and of furoic acid there is no decrease in acidity at any time during the reaction. The data for methylfurfural in table 2 show that more than 2 equivalents of acid are formed per mole of bromine consumed.

In considering the mechanism of the reaction of 1 mole of bromine with these compounds, the following conclusions may be tentatively drawn. The above experiments on acidity point to reaction IV or the sequence III to IV, in both of which 2 equivalents of hydrobromic acid are regenerated. The data for furfural exclude reaction II, in which 1 mole of acid is formed; the first and second steps in reaction III, in which 1 equivalent of hydrobromic acid is formed; and reaction V, in which 3 equivalents of acid are formed. The decided increase in acid content with methylfurfural indicates the formation of methylfuroic or other acid. In the case of furoic acid, the end point was not permanent. The figures in parentheses in the third column of table

3 indicate the amount of alkali required to maintain the end point after it was first reached. This alkali was probably consumed in neutralization of hydrobromic acid or of a keto-lactone formed in secondary steps, as in II or III. In view of the general stability of bromohydrins, and the fact that some further experiments not reported here showed that a monobromo compound is formed when furfural reacts with 2 moles of bromine under these conditions, reaction IV is preferred.

TABLE 1.—*Reaction of 1 mole of bromine with furfural in 0.1 N hydrobromic acid at 0° C*

Present at start of reaction			Acid consumed	Acid regenerated
Milligrams of furfural, 120.0	Milliequivalents of KBr-$KBrO_3$, 2.492	Milliequivalents of HBr, 2.546		
Experimental data				
Period of reaction	$Na_2S_2O_3$ used	NaOH used		
Hours	*M-eq*	*M-eq*	*M-eq*	*M-eq*
1	2.124	2.542	0.368	0.364
2	1.830	2.542	.662	.658
3	1.480	2.542	1.012	1.008
4½	1.240	2.542	1.252	1.248
6¾	0.716	2.546	1.776	1.776
9¾	.517	2.548	1.975	1.977
18[a]	.000	2.544	2.492	2.490

[a] A temperature of 0°±2° C was maintained in these experiments by use of an ice bath. In the experiment of 18 hours, the ice melted in the bath overnight with a resulting temperature slightly higher toward the end of the reaction.

TABLE 2.—*Reaction of 1 mole of bromine with methylfurfural in 0.1 N hydrobromic acid at 0° C*

Present at start of reaction			Acid consumed	Acid regenerated
Milligrams of methylfurfural, 137.0	Milliequivalents of KBr-$KBrO_3$, 2.493	Milliequivalents of HBr, 2.546		
Experimental data				
Period of reaction	$Na_2S_2O_3$ used	NaOH used		
	M-eq	*M-eq*	*M-eq*	*M-eq*
1 hr	2.170	2.550	0.323	0.327
2 hr	1.877	2.560	.616	.630
3 hr	1.667	2.562	.826	.842
4 hr	1.554	2.562	.939	.955
7½ hr	0.962	2.689	1.531	1.674
12 hr	.570	2.931	1.923	2.308
18 hr	.063	3.143	2.430	3.027
41 hr	.000	3.169	2.493	3.116

TABLE 3.—*Reaction of 1 mole of bromine with furoic acid in 0.1 N hydrobromic acid at 0° C*

Present at start of reaction			Acid consumed	Acid regenerated
Milligrams of furoic acid, 140.0	Milliequivalents of KBr–KBrO$_3$, 2.546	Milliequivalents of HBr..... 2.503 Furoic acid.. 1.255 3.758		
Experimental data				
Period of reaction	$Na_2S_2O_3$ used	NaOH used		
	M-eq	*M-eq*	*M-eq*	*M-eq*
5 min	2.481	3.743	0.065	0.050
1 hr	1.988	3.651	.558	.451
2 hr	1.424	3.557 (0.192)[a]	1.122	.921
4 hr	1.034	3.472 (.387)	1.512	1.226
6 hr	0.583	3.436 (.466)	1.963	1.641
17 hr	.038	3.390 (.519)	2.508	2.140
10 days	.000	3.687	2.546	2.475
11 days	.000	3.696	2.546	2.484

[a] Figures in parentheses represent additional amounts of alkali slowly added after the first figure was obtained for the end point. Column 5 does not include these figures.

Attempts to isolate the product of the reaction of 1 mole of bromine with 1 mole of furfural in such dilute solutions by means of extraction or steam distillation were unsuccessful. However, a precipitate is immediately formed when phenylhydrazine in acetic acid solution is added to the reaction product at 0° C. The compound crystallizes from alcohol and water as plates, which melt at 155° C. It contains no bromine, which confirms the conclusions from the acidity data. The elementary analysis [2] shows that instead of the phenylhydrazone of a dihydroxydihydrofurfural which might be expected, a dihydrazone of a hydroxy or ketodihydrofurfural is obtained. This could occur by loss of water and rearrangement as shown in reaction IV. Since the precipitation at this low temperature is immediate, it seems likely that there are two carbonyl groups ready to react with the phenylhydrazine.

Dihydrazone of a ketodihydrofurfural, $C_{17}H_{16}N_4O$ (molecular weight 292).
Calculated: C, 69.8%; H, 5.5%; N, 19.2%; O, 5.5%.
Found: C, 69.2%; H, 6.0%; N, 18.9%; O, 5.9% (by difference).

A phenylhydrazone of a dihydroxydihydrofurfural, $C_{11}H_{12}N_2O_3$, would have the following composition: C, 60.0%; H, 5.5%; and N, 12.7%. This clearly does not correspond to the compound that was obtained.

The evidence above indicates that the reaction consists in the addition of two hydroxyl ions to a positive double bond and the formation of 2 equivalents of hydrobromic acid, as in reaction IV. In this reaction the same electronic transfers as those illustrated in reaction I may take place, except that hydroxyl ions rather than bromide ions join the positive double bond. This interpretation harmonizes with the explanation given by Myers, Clarke, and Acree [6] for the electromotive force observed between ethylene and chlorine electrodes.

[2] This analysis was kindly made by C. J. Rodden, of the National Bureau of Standards.

The reaction at 0° C of equimolar quantities of furfural and bromine in water was studied. At all stages during the reaction, the experimental evidence indicates that the bromine consumed was converted quantitatively to hydrobromic acid. The product of the reaction was a hydroxy or ketodihydrofurfural, the bisphenylhydrazone of which was isolated and analyzed. With minor side reactions, methylfurfural and furoic acid behave in the same general way as furfural.

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[1] H. B. Hill and C. R. Sanger, Liebigs Ann. Chem. **232,** 42 (1885).
[2] H. Gilman and G. F. Wright, J. Am. Chem. Soc. **52,** 3349 (1930).
[3] J. B. Conant and E. L. Jackson, J. Am. Chem. Soc. **46,** 1727 (1924).
[4] O. Dimroth, E. Schultze, and F. Heinze, Ber. deut. chem. Ges. **54,** 3035 (1921).
[5] P. D. Bartlett and D. S. Tarbell, J. Am. Chem. Soc. **58,** 466 (1936).
[6] C. N. Myers, W. F. Clarke, and S. F. Acree, Phys. Chem. **20,** 286 (1916).

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STRUCTURE OF DIFRUCTOSE ANHYDRIDE III (DIFRUCTOFURANOSE 1,2′, 2,3′-ANHYDRIDE)

By Emma J. McDonald [1] and Richard F. Jackson

ABSTRACT

Difructose anhydride I, one of three isomeric difructose anhydrides derived from inulin by hydrolysis with aqueous acids, has been shown by Haworth and Streight to yield upon methylation and hydrolysis, two molecules of 3,4,6-trimethylfructose. Difructose anhydride III, upon methylation and hydrolysis, failed to yield the characteristic osazone of 3,4,6-trimethylfructose, but it was shown by oxidation to trimethylarabonolactone that this methylated fructose was one constituent of a mixture of two trimethylfructoses. Both trimethylfructoses in the mixture were shown to be furanose derivatives.

Tritylation of difructose anhydride III yielded a crystalline tritrityl derivative which was methylated to form tritrityltrimethyldifructose anhydride III. The latter was detritylated and hydrolyzed, and the products of hydrolysis were separated by fractional distillation of their methyl fructosides. The lower-boiling fraction was identified as the fructoside of 3,4-dimethylfructose, $[\alpha]_D^{20} = -60.66$, by oxidation to a 3,4-dimethyl dibasic lactol acid. The higher-boiling fraction was found to be the fructoside of 4-methylfructose, as indicated by the melting point of its glucosazone (156° C), identical with that of the osazone prepared from 4-methylglucose. The trityl groups were shown to be substituents of the three primary alcohol groups. The sugar was thus constituted of two furanoid fructose residues, with two oxygen bridges connecting carbon atoms 1 and 2 of the one residue with 2′ and 3′ of the other.

Crystalline ditrityltetra-acetyldifructose anhydride I yielded, upon methylation and hydrolysis, 3,4-dimethylfructose, and by substitution of the trityl by methyl groups, 6-methylfructose.

A mechanism is suggested by which the difructose anhydrides are formed during the hydrolysis of inulin.

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[1] The substance of this article was submitted by Emma J. McDonald to the faculty of the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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I. INTRODUCTION

In previous articles it has been shown that purified inulin yields, upon hydrolysis with aqueous acids, a mixture of sugars consisting of about 92 percent of fructose, 3 percent of glucose, and 5 percent of a group of three nonreducing difructose anhydrides [1].[2] These latter substances were found to have specific rotations of +27.0, +13.85, and +135.62, in terms of sodium light, and were designated difructose anhydrides I, II, and III, respectively. They were in each instance isolated in crystalline form.

The first of these difructose anhydrides, which was readily isolated in the form of its crystalline hexa-acetate by the procedure of Jackson and Goergen [Ia], was studied by Haworth and Streight [2], who found that its hexamethyl derivative yielded, upon hydrolysis, two molecules of 3,4,6-trimethylfructofuranose identical with that derived from fully methylated inulin. They concluded that the two fructose units were mutually linked by two oxygen bridges connecting, respectively, carbon atoms 1 and 2 of the one fructose residue with carbon atoms 2 and 1 of the other (formula *G*, page 189).

This same sugar was prepared in more than 20-percent yield from inulin acetate in chloroform solution by the action of fuming nitric acid, a reaction discovered by Irvine and Stephenson [3]. These authors, however, identified it as a monomeric anhydrofructose. Bodycote, Haworth, and Woolvin [4] showed that it was identical with Jackson and Goergen's difructose anhydride I. It is significant that only the first of the three difructose anhydrides is formed by this reaction.

It becomes important now to determine the structures of the two remaining difructose anhydrides in order to study the relations of the three sugars to one another and, if possible, their relation to inulin. It was our early expectation that the three sugars would differ in the respective configurations of the second carbon atom. If such were the case, combinations $\alpha\alpha$, $\beta\beta$, and $\alpha\beta$ would yield three different disaccharides. This view, which was also suggested by Schlubach and Knoop [5] and by Haworth and Streight [2], will be shown in the present article to be untenable.

II. HEXAMETHYLDIFRUCTOSE ANHYDRIDES AND THEIR HYDROLYSIS

Complete methylation of the three sugars caused in each case the introduction of six methyl groups. The first and third hexamethyl sugars proved to be liquids, while the second showed striking crystalline properties. All three were readily distillable in a high vacuum. The physical properties of the hexamethyldifructose anhydrides are given in table 1.

The hydrolysis was carried out in 0.8 *N* hydrochloric acid solution, the course of the reaction being followed by polarimetric observations. The hydrolysis curves of the three methylated sugars, as shown in figure 1, appeared to converge at a final specific rotation of +25° to 30°, which suggested that the product of hydrolysis was 3,4,6-trimethylfructose, whose rotation in water is +30.5°.

[1] Figures in brackets indicate the literature references at the end of this article.

TABLE 1.—*Physical properties of hexamethyldifructose anhydrides*

Difructose anhydrides	Hexamethyldifructose anhydrides											
				Boiling point		Melting point, uncorrected	$[\alpha]_D^{20}$			$[\alpha]_{5461}^{20}$		
	$[\alpha]_D^{20}$ (in water)	d_4^{20}	n_D^{20}	Pressure	Temperature		Pure liquid	In chloroform	In water	Pure liquid	In chloroform	In water
				mm	°C	°C						
I	+27.0	1.2050	1.4704	0.01	170 to 175		+19.1	+23.7	+50.4	+22.4	+27.5	+59.8
II	+13.85		[a]1.4673	.35	169 to 170	73	[a]−41.9	−28.2	+6.0		−33.4	+6.7
III	+135.64	1.1918	1.4658	.42	161 to 165		+155.7	+157.9	+164.5	+182.7	+186.9	+194.7

[a] Supercooled liquid.

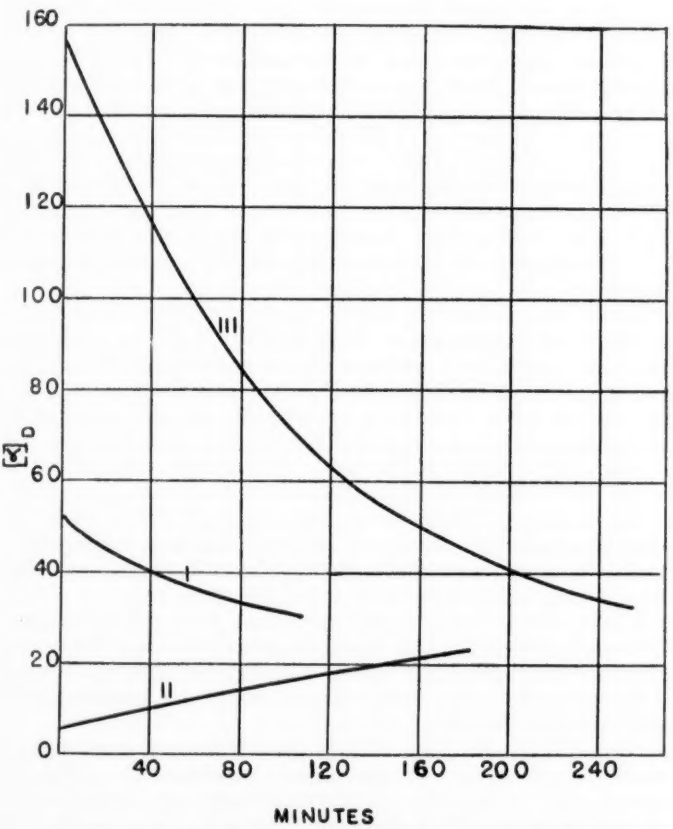


FIGURE 1.—*Hydrolysis of hexamethyldifructose anhydrides.*

The resulting samples of trimethylfructose distilled from the products of hydrolysis behaved, very differently, however, when treated with phenylhydrazine for the purpose of osazone formation. The distillate from the first sugar yielded nearly quantitatively the hydrated 3,4,6-trimethylosazone of melting point 81° C which Haworth and Learner [6] obtained from hydrolyzed trimethylinulin and Ha-

worth and Streight [2] from this same methylated disaccharide. The distillates from the second and third disaccharides, on the contrary, became discolored, and in each instance separated an oil from which but a small quantity of crystals could be separated after long standing. These crystals were so contaminated that it was found impossible to purify them sufficiently to observe their melting temperature. Our attention was thenceforth confined to the third disaccharide. The structure of difructose anhydride II will be discussed in a later article.

It seemed probable that the distillate from the third hexamethyl disaccharide consisted of two different trimethylfructoses, one of which, as suggested by the formation of osazone crystals, may have been the familiar 3,4,6. That the latter was indeed one constituent of the mixture was proved by the following experiment, in which the procedure of Haworth and Learner [6] was followed in detail.

The mixture of trimethylfructoses was oxidized by nitric acid, and the resulting mixture of monobasic acids was esterified to form the ethyl esters of the methylated lactol acids. It will be shown below that both trimethylfructoses in the mixture possessed the butylene oxide ring. Hence it is evident that, while the process of oxidation left intact the three methoxyl groups of the 3,4,6-trimethylfructose, it removed one methoxyl group from the other constituent, since any other possible trimethylfructose must bear a methoxyl group on carbon 1. The oxidized mixture then consisted of the ethyl esters of a trimethyl and a dimethyl lactol acid, the two esters having a sufficient difference in boiling point to permit a partial separation by distillation.

The lower-boiling fraction was now degraded by careful oxidation with barium permanganate in acid solution to form the trimethylarabonic acid, probably together with a smaller quantity of dimethylarabonic acid. This mixture was distilled and the lower-boiling fraction inoculated with a minute crystal of an authentic sample of trimethylarabonolactone prepared by the same oxidation processes from pure 3,4,6-trimethylfructose. Abundant crystallization followed, and the crystals when purified showed a melting point of 30° C, which was unaltered when the substance was mixed with pure trimethylarabonolactone. This methylated lactone could have been derived in the present experiment only from 3,4,6-trimethylfructose, which was consequently a constituent of the mixture.

In confirmation of our conclusion that two different trimethylfructoses were present in the distillate, condensation with acetone in the presence of sulfuric acid caused a change in rotation from 2.3° to 3.5° (saccharimeter degrees), while pure 3,4,6-trimethylfructose changed from 2.5° to 6.3°.

A portion of the mixture of trimethylfructoses was converted to their methyl fructosides and completely methylated. After removal of the fructosidic methyl group, the resulting tetramethylfructose had a specific rotation of +37°, showing that both the trimethylfructoses in the distillate belonged to the furanose series.

With the oxide ring in the 2,5 position, there are four possible trimethylfructoses; namely, 1,3,4, 1,3,6, 1,4,6, and 3,4,6. The distillate from the methylated third sugar contained as one constituent 3,4,6-trimethylfructose, together with one of the remaining three. From these, 1,3,4 can be eliminated. Hibbert, Tipson, and Brauns [7] have prepared this substance by hydrolysis of fully methylated

levan produced by the action of *Bacillus mesentericus* on cane sugar solutions. The resulting 1,3,4-trimethylfructose showed in water a specific rotation of −51.4°. If this trimethylfructose had been produced together with 3,4,6 of specific rotation +30.5° by the hydrolysis of the methylated third sugar, the rotation would have approached an end value of approximately −10°. As shown by curve III, figure 1, the end point of the hydrolysis was definitely positive; hence 1,3,4-trimethylfructose is excluded as a possible constituent. The products of hydrolysis of the methylated third sugar were then 3,4,6- and either 1,3,6,- or 1,4,6,-trimethylfructose.

Montgomery [8] synthesized 1,4,6-trimethylfructose by a chain of reactions starting from α-diacetonefructose. For the purified substance, he found a specific rotation in chloroform of +29.7°. Since 3,4,6-trimethylfructose has a rotation of +27.7° in the same solvent, the rotation of a mixture of these trimethylfructoses would not differ greatly from that of either constituent. Hence the rotation of the products of hydrolysis of the methylated third sugar would be consistent with that of a mixture of 1,4,6- and 3,4,6-trimethylfructose. 1,3,6-Trimethylfructose, however, has not been prepared and thus is not excluded as a possible constituent.

Pertinent also are the respective rotations of the acetone condensation products. Montgomery found that 3,4,6-trimethylfructose underwent a large increase in rotation upon condensation with acetone, an observation verified in the present investigation, while 1,4,6 changed but slightly. The rotation of the mixed trimethylfructoses from the methylated third difructose anhydride, upon condensation with acetone, increased by an amount roughly intermediate between that of 3,4,6- and that of Montgomery's 1,4,6-trimethylfructose.

III. TRITYL COMPOUNDS OF DIFRUCTOSE ANHYDRIDE III AND THE DERIVED PARTIALLY METHYLATED FRUCTOSES

In order that a distinction might be made between 1, 4, 6- and 1, 3, 6-trimethylfructoses, a study was made of the reaction between the difructose anhydrides and triphenylchloromethane (trityl chloride) in pyridine solution with the expectation of substituting only the primary hydroxyl groups according to the observations of Helferich and his coworkers [9]. When the procedure was applied to difructose anhydride III, difficulties arose because the preference for the primary hydroxyls apparently was not greatly in excess of that for the secondary. Nevertheless, it was possible to obtain in crystalline form a tritrityl derivative of the sugar (*B*), which indicates the probable presence of three primary hydroxyls. No conclusion, however, is drawn respecting the structure of the sugar from this reaction, but the trityl groups are definitely allocated to the primary hydroxyls by the independent argument given below.

The tritylated sugar was acetylated to form a tritrityltriacetyl derivative, which was methylated in acetone by dimethyl sulfate and sodium hydroxide to yield amorphous tritrityltrimethyldifructose anhydride III (*C*). This substance was detritylated in chloroform solution containing hydrobromic acid, and the resulting trimethyl-

difructose anhydride, together with the hydrobromic acid, was extracted with water and hydrolyzed to form a mixture of partially methylated fructoses. The latter were converted to the methyl fructosides and fractionally distilled.

The lower-boiling fraction, consisting of a methyl dimethylfructoside, was converted to a dimethylfructose of $[\alpha]_D^{20}=-60.66$ in water. The sugar was converted to its osazone, which still retained two methyl groups. This osazone was identical with that of the 3,4-dimethylfructose prepared by other methods, as described below. Oxidation with nitric acid produced a dibasic dimethyl lactol acid (*F*), whose calcium salt crystallized with four molecules of water of crystallization and contained two methyl groups. This calcium salt was evidently identical with the salt prepared by Hibbert, Tipson, and Brauns [7] from 1,3,4-trimethylfructose by the same oxidative process. The foregoing reactions, together with the demonstration that only furanose sugars are present in the disaccharide, eliminate carbons 1, 5, and 6 as positions for the introduced methyl groups, which are thus allocated to positions 3 and 4. The lower-boiling fraction was consequently the fructoside of 3,4-dimethylfructose (*E*).

The higher-boiling fraction proved to be a monomethyl methylfructoside, which, upon hydrolysis, yielded a monomethyl fructose of $[\alpha]_D^{26}=-87.5$ (at equilibrium). It yielded a monomethylglucosazone which melted at 156° C. This same osazone has been prepared from 4-methylglucose by three other groups of investigators [10], with essential agreement in the temperature of fusion. Our high-boiling fraction was therefore the fructoside of 4-methylfructose (*D*). In formulas *D* and *E*, the furanose ring is retained provisionally, since no argument can be advanced for either form in preference to the alternative.

There are but three possible monomethylfructoses which could have been formed in the present instance, since positions 1 and 5 are necessarily excluded from consideration. These are 3-, 4-, and 6-monomethylfructose. In each instance the respective glucosazone has previously been prepared, 3-methylglucosazone from 3-methylfructose, and 4- and 6-methylglucosazones from the respective methylglucoses. Inasmuch as, in the present investigation, the identification of the monomethylglucosazone from our higher-boiling fraction was of first importance for the determination of the structure of the disaccharide, we have deemed it advisable to prepare the three monomethylglucosazones in order to verify the published values of the melting points and to distinguish between them by means of mixed melting points.

3-Methylglucosazone was prepared very simply from 3-methylfructose. 6-Methylglucosazone was prepared in very pure form from 6-methylfructose, whose preparation is described below. The melting-point and mixed melting-point data are given in table 2. Evidently the low-melting point of 4-methylglucosazone distinguishes it clearly from the 3- and the 6-methylglucosazones. This is further corroborated by the depressed melting temperatures of the respective mixtures.

The rotatory power in equilibrium of the free 4-methylfructose (−87.5°) serves moreover to distinguish it from the 3-methylfructose (−53°) and the 6-methylfructose (+6.4°). Substitution on the fourth carbon atom alters the rotation of fructose much less than

substitution on the third atom, while a methyl group on carbon 6 compels the sugar to retain the furanose form.

TABLE 2.—*Melting points of substituted phenylglucosazones*

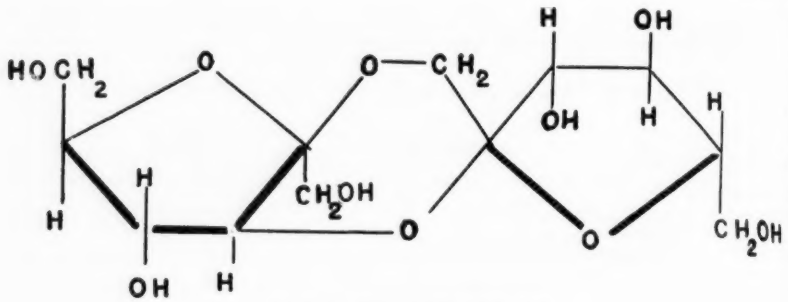
3-Methyl [11]	Melting point
	°C
Irvine and Hynd	164 to 165
Freudenberg and Hixon	178 to 179
Anderson, Charlton, and Haworth	178 to 179
McDonald and Jackson	176
4-Methyl [10]	
Pacsu	156 to 157
Munroe and Percival	158
Schinle	159
McDonald and Jackson	156
6-Methyl [12]	
Helferich and Becker	177
Ohle and Vargha	178
Kuhn and Ziese	177
McDonald and Jackson	183
Mixtures (McDonald and Jackson)	
3- and 4-Methyl	150
6- and 4-Methyl	149
3,4-Dimethyl (McDonald and Jackson)	
From inulin	126
From difructose anhydride I	126
From difructose anhydride III	* 121

* Compound not thoroughly purified.

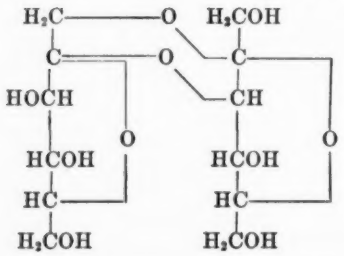
IV. STRUCTURE OF DIFRUCTOSE ANHYDRIDE III

The experimental work outlined in section II reveals that the hexamethyldifructose anhydride yielded upon hydrolysis 3,4,6-trimethylfructose and either 1,3,6- or 1,4,6-trimethylfructose. The tritylated methylated sugar yielded 3,4-dimethylfructose and 4-monomethylfructose. The 3,4-dimethylfructose was evidently derived from the same fructose residue which had yielded 3,4,6-trimethylfructose by hydrolysis of the fully methylated disaccharide. The primary alcohol on carbon 6 was therefore substituted by the trityl group in conformity with Helferich's generalization. Similarly, in the other fructose residue, since 4-methylfructose was obtained from the tritylated methylated sugar, primary alcohols on carbons 1 and 6 were substituted by trityl groups. The hexamethyl sugar thus yielded upon hydrolysis 3,4,6- and 1,4,6-trimethylfructose.

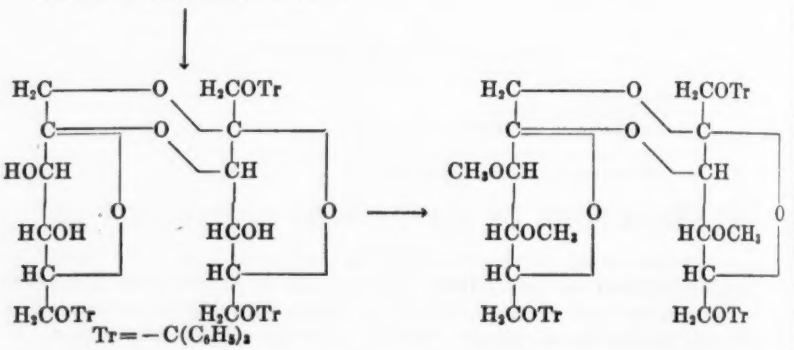
The formation of 3,4,6- and 1,4,6-trimethylfructoses requires that the two fructose residues be linked by oxygen bridges connecting positions 1 and 2 of the one fructose residue with 2′ and 3′ of the other. Two alternative combinations must be considered possible; namely, a 1,2′-2,3′ anhydride and a 1,3′-2,2′ anhydride. The former anhydride consists of two somewhat similar glycosidic unions, while the latter consists of one glycosidic and one ethereal linkage. While



(*A*) Difructose anhydride III.

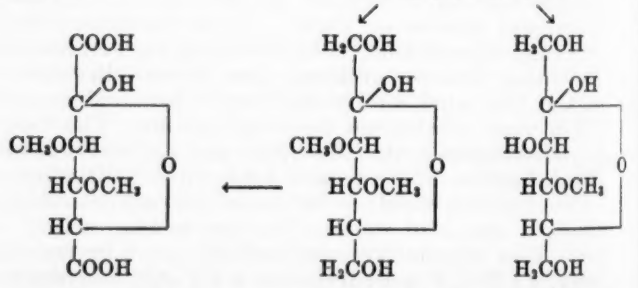


(*A'*) Difructose anhydride III.



(*B*) Tritrityldifructose anhydride III.

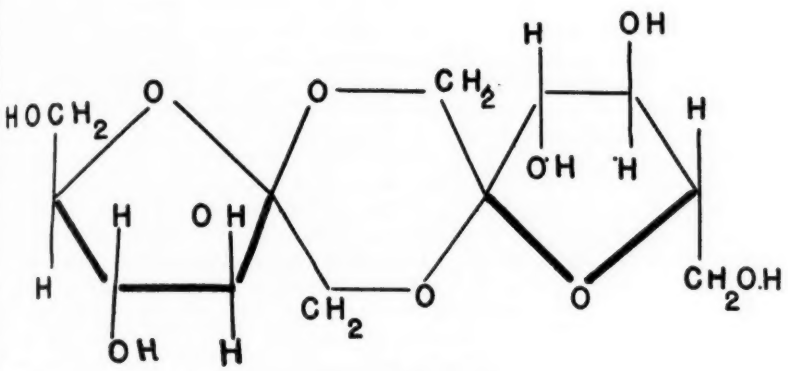
(*C*) Tritrityltrimethyldifructose anhydride III.



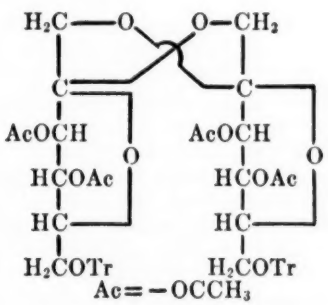
(*F*) 3,4-Dimethyl-lactol acid.

(*E*) 3,4-Dimethyl-fructose.

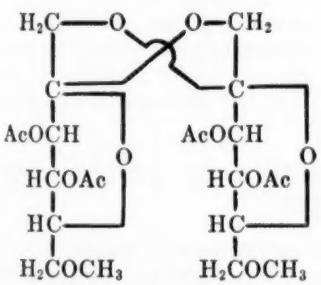
(*D*) 4-Methyl-fructose.



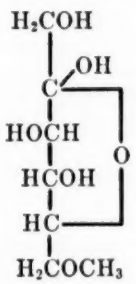
(*G*) Difructose anhydride I.



(*H*) Dityrityltetra-acetyl-difructose anhydride I.



(*I*) 6,6′-Dimethyltetra-acetyldifructose anhydride I.



(*J*) 6-Methylfructose.

two glycosidic unions would probably hydrolyze at approximately the same rate, two such fundamentally different modes of linkage as a glycoside and an ether would be expected to have widely divergent rates of hydrolysis. In point of fact, we observed some evidence of selective hydrolysis [1b], but the slight difference observed is more consistent with two glycosidic unions of slightly different structure than with the alternative. We therefore express the view that the two fructose residues are mutually linked by oxygen bridges connecting positions 1 with 2′ and 2 with 3′, respectively (*A* and *A′*).

Inspection of formula (*A*) reveals the presence of but one glycol group, while formula *G* contains two such groups. Upon treatment with periodic acid [13], 1 mole of the difructose anhydride III should therefore consume 1 mole of the oxidant, while difructose anhydride I should consume 2 moles. Experimentally, the third sugar was subjected to the action of 4 moles of periodic acid and allowed to react overnight. It was then found that 0.99 mole of oxidant had been consumed. Under similar conditions, the first disaccharide consumed 1.92 moles of periodic acid. The experimental details and the many interesting conclusions which can be derived from this oxidative reaction are reserved for a later article.

Haworth and Streight [2] have ascribed the great stability of difructose anhydride I, unusual for furanoid sugars, to the presence of the dioxane ring shown clearly in the perspective formula *G*. A similar dioxane ring constitutes the connecting link between the two fructose residues of the third sugar. The latter is, however, considerably more resistant to hydrolysis than the first disaccharide. It was shown [1a] that the first sugar in the presence of 0.2 *N* sulfuric acid hydrolyzed at 100° C with a velocity constant of 0.009. A rough calculation of data previously presented [1b] shows a velocity of hydrolysis of 0.006 for the third sugar under similar conditions. The difference in stability is greatly enhanced when the two disaccharides are methylated. No definite reason can be advanced to explain the greater stability of the third sugar, but it is to be noted that the dioxane ring in this case includes one secondary alcohol group, while the anhydro ring in the first sugar includes two primary alcohol groups. Moreover, the unknown alpha-beta relations of the constituent fructose may be a contributing factor. In none of the formulas given in this article is a distinction between alpha and beta derivatives possible at the present time and the formulas are presented with this reservation. It is our purpose to investigate these relations for the three disaccharides in continuation of the study.

V. PREPARATION AND PROPERTIES OF 3,4-DIMETHYLFRUCTOSE

It appeared desirable to prepare the unknown 3,4-dimethylfructose in more abundant quantities than could readily be obtained from difructose anhydride III, which itself was available in limited amounts. For this purpose, inulin served satisfactorily for a starting material. Under carefully determined conditions inulin was converted in pyridine solution to a monotrityl derivative and the latter acetylated by addition of acetic anhydride to the reaction mixture. The diacetylmonotritylinulin was methylated in acetone solution by addition of dimethyl sulfate and sodium hydroxide and the methylated

compound obtained in the form of an amorphous powder. The substance was detritylated, hydrolyzed, and converted to acetonedimethylfructose in a single operation by dissolving in acetone and adding sulfuric acid. The acetonedimethylfructose was isolated by distillation, converted to methyl dimethylfructoside, which received a final purification by fractional distillation. Some uncertainty was inherent in this procedure arising from the possibility that tritylation may have been incomplete and thus partial methylation may have produced other dimethyl derivatives than the one desired.

This uncertainty was eliminated by utilizing difructose anhydride I as a source. This sugar, upon tritylation and acetylation, yielded a ditrityl tetra-acetyl derivative (*H*), which proved to be crystalline and lent itself to thorough purification. The tetramethyl derivative prepared by the action of dimethyl sulfate and sodium hydroxide was amorphous and was detritylated and hydrolyzed without further purification. The resulting dimethylfructose was purified by two distillations as methyl dimethylfructoside. The free sugar was obtained upon removal of the fructoside group.

The purified 3,4-dimethylfructose obtained from difructose anhydride I proved to be a viscous liquid of $[\alpha]_D^{20} = -60.66$ in water. It formed a crystalline osazone which melted at 126° C. Its structure is fairly indicated by its method of synthesis. Oxidation by nitric acid converted it to the dibasic 3,4-dimethyl lactol acid whose calcium salt has been described above. The free sugar obtained in the form of a sirup has thus far failed to crystallize. Upon removal of the solvent, the sugar showed a strong tendency to polymerize. This dimethyl sugar will be studied further.

VI. 6-METHYLFRUCTOSE

Ditrityltetra-acetyldifructose anhydride I (*H*) was detritylated in acetic acid solution by addition of hydrogen bromide, yielding a crystalline tetra-acetyl derivative, which was methylated by Purdie's reagents to form crystalline dimethyltetra-acetyldifructose anhydride I (*I*). This was deacetylated and hydrolyzed in one step, and the resulting sugar converted to its methyl fructoside and distilled. Upon removal of the fructoside group, the sugar (*J*) showed an equilibrium rotation ($[\alpha]_D^{26}$) of +6.4 and yielded an osazone melting at 183° C. This interesting derivative will receive further attention in a later article.

That the methyl group was situated on the sixth carbon atom follows from the fact that the same ditrityltetra-acetate (*H*) yielded ditrityltetramethyldifructose anhydride I from which 3,4-dimethylfructose was obtained. The trityl groups thus occupied the sixth position, and since in the formation of the dimethyltetra-acetate the methyl groups have replaced the trityl groups, they too occupy position 6. The melting point and rotation of the osazone, which are in fair agreement with the data respecting the osazone prepared from 6-methylglucose, make it probable that no migration of acetyl groups occurred during the various steps of the preparation.

VII. ORIGIN OF THE DIFRUCTOSE ANHYDRIDES

In our earlier article we expressed the view that the difructose anhydrides were integral parts of the inulin molecule, and on account of their high stability survived the hydrolysis. This idea, which was

enunciated before anything was known concerning the structures of the sugars and which indeed has encountered much adverse criticism, appears now definitely incorrect. An alternative view is suggested.

We may suppose that during the process of hydrolysis the inulin aggregate is ruptured at various points, leaving shortened chains, each fragment having a free reducing group at one end. In a relatively small number of instances the hydroxyl of the terminal reducing group apparently condenses with one of the hydroxyls of the penultimate fructose residue, thus forming a difructose anhydride entity which becomes so stable as to resist further hydrolysis. This condensation of one fructose residue with a closely contiguous residue is in keeping with the known tendency of fructose derivatives to polymerize. On the penultimate fructose residue, carbon atoms 3, 4, and 6 bear hydroxyls which are available for this condensation, and the union through an atom of oxygen of carbon atom 3 with carbon 2 of the terminal residue would lead to the formation of difructose anhydride III, whose structure has been discussed above. This condensation clearly can occur at any time before the complete resolution of the inulin fragments to individual fructose units, but not after, since we have shown in a previous article [1a] that fructose itself is not appreciably altered under the conditions of inulin hydrolysis. Difructose anhydride I, on the other hand, can only be formed by the momentary isolation of a fragment consisting of two fructose residues, followed by condensation or, obviously, by the simultaneous hydrolytic splitting of the fragment and condensation to the anhydride. This latter case is evidently what occurs during the course of Irvine and Stephenson's reaction of inulin acetate in chloroform solution with nitric acid. It is now clear why the first anhydride only is formed by this reaction, since the remaining carbon atoms are already substituted by acetyl groups.

The condensation to the anhydride in the cases of the two sugars whose structures are known occurs without the shifting of the oxide ring to the normal form. Whether mutarotation occurs is of course undetermined. If both mutarotation and ring shift can occur before condensation to the anhydride, the number of possible difructose anhydrides capable of formation during the hydrolysis of inulin becomes very large.

A considerable number of difructose anhydrides has already been reported, some prepared 5y depolymerization of inulin, some by synthesis, and some are of natural occurrance. It is interesting to note that all are anhydrousugars and all are nonreducing.

We have already learned that difructose anhydride II is, like III, unsymmetrically constructed and probably accounts for one of the remaining possible structures. Moreover, during the preparation of the three crystalline sugars we have accumulated a considerable quantity of mother liquors which show the same high resistance to hydrolysis, but which fail to crystallize, even when abundantly inoculated with crystals of those already isolated.

Schlubach and Knoop [14] have by exhaustive fractionation separated the polysaccharides occurring in the jerusalem artichoke into three main constituents; namely, inulin, a dilevan, and a positively rotating difructose anhydride. The latter substance, even after several hundred operations, was not obtained in a pure state but was methylated and isolated by fractional distillation of its hexamethyl

derivative. They suggest that this disaccharide is identical with our difructose anhydride III, and indeed the high rotatory power of their hexamethyl sugar, +149° in chloroform, as compared with our value, +158°, for the highly purified substance makes this seem plausible. They report, however, that the properties of the products of hydrolysis agree with those of 3,4,6-trimethylfructose and that an osazone of melting point 77° to 79° C was formed. The essential question whether this osazone was formed in nearly quantitative yield as it is from methylated inulin is not discussed. We too obtained the crystalline 3,4,6-osazone, as stated above, but in such small yield that we were led to the conclusion that it was formed from but one of the fructose residues in the disaccharide. If their osazone was formed in good yield, it follows that the two disaccharides are different. If formed in poor yield, the question remains undetermined.

The difficulty of separation of their difructose anhydride from inulin is quite at variance from our experience. One gram of our third sugar was dissolved in a hot-water solution of 10 g of inulin and the solution allowed to cool. Upon crystallization of the inulin and filtration, the sugar appeared practically quantitatively in the mother liquor.

Schlubach and Knoop [14] also suggest that our difructose anhydride II is perhaps the same as the synthetic disaccharide which Schlubach and Elsner [15] obtained by the action of acetone on fructose in the presence of hydrochloric acid. Their sirupy hexamethyl sugar, however, showed a rotation of +31° in chloroform, while ours, a crystalline substance, showed −28°. Moreover, their substance was hydrolyzed to 3,4,6-trimethylfructose by the mild action of oxalic acid, while our second sugar requires the prolonged action of hydrochloric acid at nearly boiling temperature. Indeed, it is the most stable of the three difructose anhydrides which we have described. In contrast to Schlubach and Elsner's methylated sugar, the products of hydrolysis in this case are not exclusively 3,4,6-trimethylfructose.

VIII. EXPERIMENTAL

1. HEXAMETHYLDIFRUCTOSE ANHYDRIDES

The procedure devised by Haworth [16] was employed for the methylation of the three crystalline sugars; namely, solution in the minimum quantity of water and successive additions of methyl sulfate and 30 percent sodium hydroxide at 70° C. The sirupy product was soluble in methyl iodide and the methylation was completed by use of methyl iodide and silver oxide in the usual manner. Since only the first difructose anhydride formed a crystalline acetate, additional preparations of its hexamethyl compound were made by direct methylation of the acetate in acetone solution by means of methyl sulfate and 30 percent sodium hydroxide [17].

Hexamethyldifructose anhydride I.—This substance formed a slightly viscous, nearly colorless liquid which distilled at about 170 to 175° C and 0.01-mm pressure. $d_4^{20}=1.2050$; $n_D^{20}=1.4704$; $[\alpha]_D^{20}=+19.1$ (pure liquid), +23.7 (chloroform, $c=4.861$), +50.4 (water, $c=1.614$); $[\alpha]_{5461}^{20}=+22.4$ (pure liquid), +27.5 (chloroform, $c=3.13$), +59.8 (water, $c=1.614$). Haworth and Streight [2] gave the values, $n_D^{16}=1.4719$; $[\alpha]_D^{20}=+24$ (chloroform), +53 (water). *Analysis.* Calculated for $(C_9H_{16}O_5)_2$: OCH_3, 45.6. Found: 44.3.

Hexamethyldifructose anhydride II.—This derivative crystallized spontaneously even before it was completely extracted from the silver compounds. Upon recrystallization, it took the form of large polyhedra. One preparation formed a single crystal 2 cm in length. Melting point, 73° C (uncor.); $n_D^{20}=1.4673$ (supercooled liquid); $[\alpha]_D^{20}=-41.9$ (pure supercooled liquid), −28.2 (chloroform, $c=3.555$), +6.0 (water, $c=3.735$); $[\alpha]_{5461}^{20}=-33.4$ (chloroform, $c=3.555$), +6.7 (water, $c=3.735$). It distilled at 169° to 170° C at 0.43 mm, bath temperature, 190° C. *Analysis.* Calculated for $(C_9H_{16}O_5)_2$: OCH_3, 45.6. Found: 45.6.

Hexamethyldifructose anhydride III.—The methylated third sugar formed a fairly mobile liquid which distilled at 161° to 165° C at 0.417 mm from a bath at 183° to 193° C. $d_4^{20}=1.1918$; $n_D^{20}=1.4658$; $[\alpha]_D^{20}=+155.7$ (pure liquid), +157.9 (chloroform, $c=3.95$), +164.5 (water, $c=2.232$); $[\alpha]_{5461}^{20}=+182.7$ (pure liquid), +186.9 (chloroform, $c=3.95$), +194.7 (water, $c=2.232$). *Analysis.* Calculated for $(C_9H_{16}O_5)_2$: OCH_3, 45.6. Found: 45.0.

2. HYDROLYSIS OF THE HEXAMETHYLDIFRUCTOSE ANHYDRIDES

Hexamethyldifructose anhydride I was hydrolyzed in the manner described by Haworth and Streight [2]; namely, by digestion with 0.8 *N* hydrochloric acid at 95° C to constant rotation. The course of the hydrolysis is shown in figure 1. The solution was neutralized with barium carbonate, evaporated to dryness in the presence of barium carbonate, extracted with ether, and distilled under 0.2-mm pressure. The 3,4,6-trimethylfructose, upon treatment with phenylhydrazine, formed the hydrated osazone (melting point, 81° C) in nearly quantitative yield.

Hexamethyldifructose anhydride III presented greater difficulty than the first sugar because of its greater resistance to hydrolytic action. In exploratory experiments it was ascertained that under the conditions necessary to approach complete hydrolysis furfural derivatives accumulated to such an extent as to interfere seriously with the purification of the trimethylfructose. Indeed, it was at first considered probable that the failure to obtain the characteristic osazone was due to excessive contamination by furfural derivatives.

The rate of destruction of 3,4,6-trimethylfructose under the conditions of hydrolysis was measured by subjecting a sample, prepared from trimethylinulin, to 0.8 *N* hydrochloric acid at 95° C. By a calculation based upon its initial and final rotations, it was determined that the substance had decomposed 13 percent in 1 hour. Hexamethyldifructose anhydride III was 50 percent hydrolyzed in 91 minutes and 70 percent in 157 minutes.

From these data it was roughly calculated that if the hexamethyl sugar were hydrolyzed for three periods of 91 minutes each and the trimethylfructose were removed by distillation after each period of hydrolysis, about 88 percent of the sugar would be hydrolyzed and that about 10 percent of the trimethylfructose thus formed would be destroyed. Should the acid hydrolysis consist of two consecutive treatments of 157 minutes each, 91 percent of the hexamethyl sugar would be hydrolyzed and about 20 percent of the trimethylfructose would be destroyed. It was, therefore, decided to hydrolyze the methylated sugar in three periods of 91 minutes each and to remove the trimethylfructose by distillation after each period. In order to

keep the still residue undamaged, the bath temperature was held as low as possible. This necessitated the use of an ineffective fractionating column, and the unhydrolyzed substance tended to distill over in appreciable quantities.

A sample (7.23 g) of the third hexamethyl sugar was hydrolyzed for 91 minutes at 95° C. The acid was neutralized with barium carbonate, and the filtrate was evaporated and extracted with chloroform. From the products of hydrolysis there were obtained a distillate, *A*, (3.42 g) of $[\alpha]_D = +50.4$, and a still residue. The latter was hydrolyzed and yielded a distillate, *B*, (1.72 g) of $[\alpha]_D = +30.0$. Distillates *A* and *B* were combined and redistilled, yielding distillate *C* (3.87 g) of $[\alpha]_D = +26.6$, and a still residue which was combined with that from *B* and again hydrolyzed and distilled, yielding a distillate, *D*, (0.71 g) of $[\alpha]_D = +29.1$. Recovered as trimethylfructose, 4.58 g. The combined distillates were dissolved in water and titrated at 10° C with neutral dilute permanganate until a spot test with a potassium iodide-starch solution showed that furfural derivatives had been completely oxidized. The solution was treated with carbon, filtered, evaporated, and the trimethylfructose redistilled.

When a small sample of the trimethylfructose was treated with phenylhydrazine in dilute acetic acid solution, the reaction mixture turned brown and deposited an oil, which was washed and dissolved in alcohol. After long standing, the solution deposited a relatively small amount of crystals, which were so highly contaminated with oily material that it was found impossible to purify them.

The mixture of trimethylfructoses was oxidized in two stages by nitric acid and by permanganate, respectively, and thus degraded to trimethylarabonolactone (melting point, 31° C), the procedure described by Haworth and Learner [6] being followed in detail.

3. TRITYL DERIVATIVES OF DIFRUCTOSE ANHYDRIDE III

Tritrityldifructose anhydride III.—The tritylation of the third sugar proved to be difficult, and the yields of tritritylated sugar were small. The difficulty arose from the fact that, except under a narrow range of conditions, the desired tritrityl sugar was merely one stage in the succession of reactions and that this product was accompanied by under- and over-tritylated sugar. This appears to be one of the few cases in which the preference of the trityl group for the primary alcohol is not greatly in excess of that for the secondary. Fortunately the tritrityl sugar was the only definitely crystalline product and could thus be purified and accepted as homogeneous. The course of the condensation was followed by polariscopic observation, the rotation reaching a maximum at about 1.7 times the initial value and thereafter diminishing, probably as a result of substitution of secondary alcohol groups.

Yields of 40 to 45 percent of crystalline tritrityl sugar were obtained by the following procedure. Any considerable departure from that described caused the formation of over- or under-tritylated products. Two and one-half grams of the dried sugar was dissolved in 32 ml of redistilled pyridine and 7.2 g of trityl chloride was added (11 percent in excess of theory). The solution was heated in a glycerin bath at 80° C for ½ hour and allowed to stand overnight at room temperature. Water was added to slight turbidity, and the carbinol-pyridine complex which crystallized was removed by filtration. The

filtrate was poured into water and the separated substance collected on a filter, washed, and air-dried. The dried substance retained a considerable amount of pyridine, which it was found necessary to volatilize completely.

The final product was recrystallized in the form of fine needles to constant properties from methyl alcohol containing 5 to 10 percent of acetone. Melting point, 127° C (uncor.); $[\alpha]_D = +64.2$ (chloroform, $c=0.76$). Triphenylcarbinol [18], calculated; 74.3. Found: 73.1.

Tritrityltriacetyldifructose anhydride III.—The acetylation of the tritrityl sugar was effected very simply by the usual procedure. In 5 ml of pyridine was dissolved 0.73 g of tritrityldifructose anhydride III, 5 ml of acetic anhydride was added, and the mixture was heated on the steam bath for 1 hour. After standing overnight at room temperature, it was poured into a large volume of water from which it was recovered quantitatively. For purification, it was dissolved in warm absolute alcohol and allowed to separate slowly during partial evaporation of the solvent. The substance proved to be amorphous. $[\alpha]_D = +65.2$ (chloroform, $c=0.71$).

The analysis of the product proved difficult and unsatisfactory. Determination of acetyl groups [19] was made by refluxing the sample with standard alcoholic potash, followed by back titration with standard hydrochloric acid. Calculated for three acetyl groups: $OCCH_3$, 10.97. Found: 10.95, 10.65, 10.51. Duplicate determinations varied, however, frequently by as much as 10 percent of the quantity measured. The analytical data, although no criterion of the purity of the substance, proved definitely the presence of three acetyl groups, since four acetyl and two trityl groups would have required 17.62 percent of acetyl, while two acetyl with four trityl groups would have required 6.25 percent of acetyl.

Tritrityltrimethyldifructose anhydride III.—In 100 ml of acetone, 3.68 g of tritrityl triacetyl sugar was dissolved, and the mixture was agitated vigorously at 55° C with a motor-driven stirrer. In 10 equal portions total volumes of 36 ml of dimethyl sulfate and 96 ml of a 30-percent sodium hydroxide solution were added, together with additional quantities of acetone, the methylation requiring about 2½ hours. The reaction mixture was poured into a large volume of violently agitated water and the precipitated substance filtered and air-dried. Crude yield, 3.42 g, or 100 percent of theory. The substance was dissolved in acetone and fractionally precipitated by slow addition of absolute alcohol. Yield, 2.315 g. $[\alpha]_D^{24} = +70.2$ (chloroform, $c=1.05$). Calculated: OCH_3, 8.51. Found: 8.49.

4. DETRITYLATION AND HYDROLYSIS OF TRITRITYLTRIMETHYLDIFRUCTOSE ANHYDRIDE III

The isolation of the partially methylated fructoses from the tritrityltrimethyldifructose anhydride III was accomplished and repeated several times from different preparations of the substance with uniform results. Typically, 6.9 g of substance in a small Claissen flask was dissolved at 0° C in 130 ml of chloroform containing 2.66 g of anhydrous hydrogen bromide. The solution was allowed to remain at this temperature for about 1 hour, after which 20 ml of water was added and the chloroform distilled off under diminished pressure, leaving the methylated sugar and acid in water solution and the triphenylcarbinol in suspension. The latter was removed by filtra-

tion and extracted with 3-ml portions of water until 41 ml of filtrate had accumulated. The solution was at this point about 0.8 *N* with respect to hydrobromic acid. The methylated sugar was hydrolyzed for 2½ hours at 94° C, during which time the rotation (2-dm column) changed from +36.9 to −12.6 (saccharimeter degrees). The acid was removed with silver carbonate and the filtrate treated with hydrogen sulfide. The filtered solution was freed from hydrogen sulfide and treated at 10° C with neutral dilute potassium permanganate until a starch-iodide test showed the oxidation of oxidizable impurities to be complete, the equivalent of 15 ml of 0.1 *N* potassium permanganate being required. The solution was treated with a small amount of carbon, filtered, and evaporated to dryness, the residual solvents being removed by evacuation with a mercury-vapor pump.

The sirup was dissolved in 100 ml of dry methyl alcohol containing 0.5 g of hydrochloric acid and allowed to stand overnight. The acid was removed with silver carbonate and the filtrate evaporated.

The mixed fructosides were distilled from a small flask with a 70-mm still head. The lower-boiling fraction (0.578 g) distilled (<0.01 mm) at a bath temperature of 147° to 156° C. The higher-boiling fraction (0.651 g) was recovered at 156° to 170° C by immersing the entire still head in the bath. The still residue was transferred to a smaller flask and yielded an additional distillate of 0.244 g. Total distillate recovered, 1.474 g, or 54 percent of the theory.

The bath temperatures given above do not reveal the difference in boiling point of the two fractions. In another experiment the mixed fructosides were distilled from a small retort, the condenser arm of which was but 3 mm above the bath. The lower-boiling fraction distilled at a bath temperature of 134° to 140° C and the second fraction at 164° to 170° C at less than 0.01-mm pressure. There was thus about 30° C difference in boiling point.

The loss of nearly 50 percent of the hydrolysis products is readily explained. The methylated disaccharide was necessarily incompletely hydrolyzed, the partially methylated fructoses were severely attacked under the conditions of hydrolysis, the sugars were to some extent adsorbed by carbon, and an inevitable retention in the distilling vessel occurred.

Both fractions were redistilled, a considerable intermediate portion being discarded in order to insure the purities of the remaining fractions.

3,4-Dimethylfructose.—The lower-boiling fraction was a methyl dimethylfructoside. Calculated: OCH_3, 41.9. Found: 40.7.

A sample (0.5486 g) was dissolved in 11.4 ml of 0.1 *N* hydrochloric acid and hydrolyzed at 60° C for 1 hour. A parallel experiment had shown that hydrolysis was complete under these conditions and that the rotation changed from a positive value to an approximately equal negative value. To the cooled solution silver carbonate from 0.4 g of silver nitrate was added and the volume made up to 25.413 ml. A calculated volume of 0.052 ml for the precipitated silver chloride and excess silver carbonate was deducted. The filtered solution containing 0.5140 g of dimethylfructose showed $[\alpha]_D^{27} = -53.64$ ($\alpha = -6.28$, 2-dm column, saccharimeter degrees). For a sample of pure 3,4-dimethylfructose prepared as described below, $[\alpha]_D^{27} = -53.59$.

The solution, treated with phenylhydrazine in dilute acetic acid solution, deposited crystals of dimethylglucosazone, but difficulty was encountered in purification. The observed melting point, 121° C,

after recrystallization was somewhat lower than that, 126° C, of the more highly purified substance obtained by other methods of preparation. Its identity was proved beyond question by examination of the product of oxidation by nitric acid, the procedure described by Hibbert Tipson, and Brauns [7] being followed in detail.

Oxidation of 3,4-dimethylfructose.—One gram of methyl 3,4-dimethylfructoside was treated with 6 ml of concentrated nitric acid (*d*, 1.42) in a cool water bath, the temperature of which was gradually increased. At about 65° C gas evolution became vigorous, and the solution was kept at this temperature until the reaction had subsided. The temperature was then slowly raised to 95° C during a period of 1½ hours from the beginning of the reaction. The solution was cooled, diluted with 5 volumes of water, and evaporated under diminished pressure with continuous additions of water until eventually the final portion of distillate was approximately free from nitric acid. The thick yellow liquid consisting of dimethyl lactol acid was diluted with water, and the solution boiled with an excess of calcium carbonate. The filtered solution which was allowed to evaporate spontaneously slowly deposited polyhedral crystals. These were recrystallized from hot water and were evidently identical with the substance which Hibbert, Tipson, and Brauns derived from 1,3,4-trimethylfructose. Calculated for $C_8H_{10}O_8Ca.4H_2O$: H_2O, 20.8. Found: 19.9. Calculated for $C_8H_{10}O_8Ca$: OCH_3, 22.5; Ca, 14.57. Found 22.44, 14.79.

4-Methylfructose.—A portion of the higher-boiling fraction containing methyl monomethylfructoside equivalent to 65.6 mg of methylfructose was dissolved in 5.8 ml of 0.1 *N* hydrochloric acid and hydrolyzed for 1 hour at 60° C. Silver carbonate from 0.2 g of silver nitrate was added and the solution made to a volume of 17.228 ml, from which a computed volume of 0.026 ml for the silver salts was deducted. The filtered solution rotated −1.93° S (2-dm column, saccharimeter degrees); whence $[\alpha]_D^{26}=-87.5$ ($c=0.387$). The same solution, after treatment with hydrogen sulfide and evaporation yielded a crystalline phenylosazone, which after recrystallization melted sharply at 156° C. Calculated for $C_{19}H_{24}O_4N_4$: OCH_3, 8.4; N, 15.05. Found: 8.6, 15.05.

Mixture of the 4-methyl with 3-methylglucosazone depressed the melting point to 150° C, and with 6-methylglucosazone to 149° C.

5. 3,4-DIMETHYLFRUCTOSE

Trityldiacetylinulin.—Inulin (10 g), previously dried overnight at 80° C and 2 hours at 120° C, was swollen in 200 ml of freshly distilled pyridine. Thirty grams of trityl chloride was added in small portions, causing usually the precipitation of inulin, which redissolved upon gentle warming. The mixture was agitated for 4 days at room temperature and then heated to 90° C for 1 hour. After it was cooled, 80 ml of acetic anhydride was added, and the mixture was heated at 65° C for 1 hour and at 110° C for ½ hour. To the cooled solution water was added dropwise to slight turbidity, and the crystals, which formed slowly, were separated by filtration. The filtrate was poured into a large volume of water with vigorous agitation. Trityldiacetylinulin, together with triphenylcarbinol, separated as a white precipitate. This was purified by separation as an amorphous powder from absolute alcohol. Yield, 8 g. $[\alpha]_D^{21}=+13.1$ ($c=1.22$, chloroform). Triphenylcarbinol, calculated: 53.4. Found: 53.3.

Trityldimethylinulin.—Seven grams of trityldiacetylinulin was dissolved in 250 ml of acetone. In 10 portions at 10-minute intervals total volumes of 120 ml of dimethyl sulfate and 320 ml of 30-percent sodium hydroxide were added. During the reaction, the solution was vigorously stirred and maintained at a temperature of 55° C. The reaction mixture was poured into a large volume of water which was vigorously agitated. The precipitated trityldimethylinulin was purified by separation as an amorphous powder from a methyl alcohol solution. Yield, 6.5 g, or 82 percent of theory. Calculated: OCH_3, 14.4. Found: 15.3.

No high degree of purity can be claimed for the tritylated derivatives of inulin, but they have the advantage of yielding abundant quantities of partially methylated fructose from readily available materials.

3,4-Dimethylfructose from trityldimethylinulin.—Ten grams of trityldimethylinulin was dissolved in 250 ml of acetone. Five milliliters of concentrated sulfuric acid was added, and the mixture was allowed to stand overnight at room temperature. Dry ammonia gas was passed into the solution and the precipitated ammonium sulfate separated by filtration and washed with acetone. The acetone was evaporated in the presence of barium carbonate, and the residue was extracted repeatedly with warm water. The water was evaporated, leaving a sirupy residue, which was subjected to fractional distillation at a pressure of 0.2 mm. At a bath temperature of about 80° C, β-diacetonefructose sublimed and crystallized. This was followed by acetone condensation products at about 100° C. The main fraction boiling at a bath temperature of about 115° to 130° C consisted principally of monoacetonedimethylfructose. This fraction was redistilled, yielding three approximately equal fractions, *A* (bath, 117° to 121° C; inside, 99° to 101° C; OCH_3, 24.4); *B* (bath, 122° to 126° C; inside 101° to 106° C; OCH_3, 23.1); and *C* (bath, 125° to 131° C; inside, 105° to 110° C; OCH_3, 21.6). Theory for monacetonedimethylfructose: OCH_3, 25.0. The fractions were converted separately to the methyl fructosides.

Monoacetonedimethylfructose (6.2 g) was dissolved in 100 ml of 95-percent alcohol and made to 150 ml with water containing 0.18 g of hydrochloric acid, according to the procedure of Irvine and Hynd [11]. Hydrolysis of the acetone group was effected by heating in a boiling-water bath for about 1½ hours, during which time the rotation changed from −5.25° to −7.90° (2 dm, saccharimeter degrees). The acid was removed by means of silver carbonate followed by hydrogen sulfide in the usual manner. The filtrate was evaporated to dryness and dissolved in dry methyl alcohol containing 5 mg of hydrochloric acid per milliliter. During the formation of the fructoside, the initial negative rotation changed to a positive value slightly more than twice as great in the course of 3 hours. The reducing power became practically zero.

The dimethylfructose prepared by this method was invariably contaminated by monomethylfructose, which probably consisted mainly of 4-methylfructose, since 3-methylfructose, if present, was largely eliminated in the form of the low-boiling 3-methyldiacetonefructose. The separation of methyl dimethylfructoside from methyl monomethylfructoside by fractional distillation was not difficult, since there was a difference of about 30° C in boiling point. The dimethyl

derivative distilled at 0.01 mm at a bath temperature of 132° C. The substance, after hydrolysis, showed the same properties as the dimethylfructose prepared from the more reliable ditrityltetramethyldifructose anhydride I and yielded the same osazone melting at 126° C.

In one experiment, trityldimethylinulin was detritylated by dissolving it in chloroform and adding a chloroform solution of hydrogen bromide. The substance was detritylated effectively, but the dimethylinulin was apparently depolymerized in great part to difructose anhydrides, which subsequently required vigorous conditions of acidity and temperature for hydrolysis. This depolymerization to difructose anhydride is evidently analogous to Irvine and Stevenson's depolymerization with nitric acid.

Ditrityldifructose anhydride I.—One gram of sugar and 3 g of trityl chloride were dissolved in 15 ml of redistilled pyridine and allowed to remain at room temperature for 3 days. Water was added to slight turbidity, and, after the mixture was cooled to 0° C, the carbinol-pyridine complex was removed by filtration. The filtrate was poured into a large volume of ice water and the resulting white gummy precipitate washed and air-dried. From warm methyl alcohol the substance crystallized as fine needles, which were recrystallized to constant properties. Yield, 1.05 g, or 42 percent of theory. Melting point, 195° C (uncor.); $[\alpha]_D^{22}=+20.35$ (chloroform, $c=2.186$). Triphenylcarbinol, calculated, 64.4. Found: 64.4.

Ditrityltetra-acetyldifructose anhydride I.—In 120 ml of pyridine were dissolved 6.3 g of sugar and 18 g of trityl chloride. The mixture was allowed to remain at room temperature for 3 days and was then heated to 85° to 90° C for 1 hour. The solution was cooled and 60 ml of acetic anhydride added. The mixture was heated at 70°C for 1 hour and finally at 110° C for ½ hour. When the mixture was cool, water was added to slight turbidity and the carbinol-pyridine crystals separated by filtration. The filtrate was poured into a large volume of ice water. The precipitate which formed was dried and dissolved in warm absolute alcohol, from which the substance separated as transparent spheroids. Upon repeated recrystallization from absolute alcohol, ditrityltetra-acetyldifructose anhydride I appeared as needle-like crystals. Yield, 14.7 g, or 92 percent of theory. Melting point, 194° C (uncor.); $[\alpha]_D^{20}=+21.06$ (chloroform, $c=3.731$). Triphenylcarbinol, calculated, 53.3. Found: 52.5. Acetyl ($OCCH_3$), calculated, 17.6. Found: 18.0.

A portion of this compound was used for the preparation of 3,4-dimethylfructose and the remainder for 6-methylfructose.

Ditrityltetramethyldifructose anhydride I.—In 150 ml of acetone was dissolved 5.29 g of ditrityltetra-acetyldifructose anhydride I, and the solution was heated to 55° C. In 10 equal portions at intervals of 15 minutes, total volumes of 54 ml of dimethyl sulfate and 144 ml of 30-percent sodium hydroxide were added with vigorous agitation by a motor-driven stirrer. The reaction mixture was poured into water and the precipitate collected and dried. The substance was amorphous. OCH_3, calculated, 14.35. Found: 14.65.

3,4-Dimethylfructose.—Ditrityltetramethyldifructose anhydride I (6.8 g) was dissolved in chloroform and cooled to 0° C. A solution of 2.5 g of hydrogen bromide in chloroform was added and the mixture allowed to stand for about 1 hour. There was added 25 ml of water

and the chloroform was evaporated at diminished pressure, leaving the tetramethyl disaccharide and hydrobromic acid in water solution with the insoluble triphenylcarbinol in suspension. The soluble materials were filtered, and the precipitate was washed. The combined filtrate and washings (65 ml) were made 0.8 *N* with hydrogen bromide and some additional hydrochloric acid, and the sugar was hydrolyzed for 2 hours at 95° C, during which time the rotation changed from +6.5 to −8.5° (2-dm column, saccharimeter degrees). The acids were neutralized with silver carbonate and the filtrate was treated with hydrogen sulfide. The filtered solution was evaporated and the substance converted to the methyl fructoside by dissolving in dry methyl alcohol and adding a methyl alcohol-hydrogen chloride solution, the final concentration of acid being 5 mg per milliliter. During fructoside formation, the rotation changed in 3½ hours from −40.1° to +8.27° (2-dm column, saccharimeter degrees), passing through zero in 7 minutes. Another preparation of this fructoside from monotrityldimethylinulin showed the same relative change of rotation, but on standing for a longer period the positive rotation diminished considerably. However, unlike that of unsubstituted fructose, its final rotation remained definitely positive even after several days.

The fructoside distilled at 0.01 mm at 100° C; bath temperature, 131° C. Calculated: OCH_3, 41.9. Found: 40.0. The substance was dissolved in water at 10° C and treated with neutral dilute potassium permanganate until a starch-iodide test showed the oxidation of impurities to be complete. It was filtered through carbon and redistilled at 0.01-mm pressure. The substance distilled completely at a bath temperature of 129° to 130° C. Calculated: OCH_3, 41.9. Found; 41.5.

The purified fructoside was dissolved in about 30 parts of 0.1 *N* hydrochloric acid. Hydrolysis was complete in 1 hour at 60° C, during which time the rotation changed from +12.75° to −11.58° (saccharimeter degrees). The acid was removed with silver carbonate in the usual manner. An effort was made to determine the properties of the dimethyl sugar, but during the drying the substance apparently polymerized. In another experiment 0.2047 g of fructoside, equivalent to 0.1918 g of dimethylfructose, was hydrolyzed in a small volumetric flask in 11.4 ml of 0.1 *N* hydrochloric acid, and the acid was neutralized with silver carbonate derived from 0.4 g of silver nitrate. The solution containing the precipitate was made to a volume of 25.396 ml at 20° C, and the volume of silver chloride and excess silver carbonate was computed to be 0.052 ml. The rotation of the filtered solution was carefully measured at several temperatures, the expansion being calculated by assuming a coefficient of 0.00025. $[\alpha]_D^t = -60.66 + 1.01(t - 20°\ C)$; whence $[\alpha]_D^{20} = -60.66$ (water, $c = 0.757$).

The 3,4-dimethylfructose was converted into a crystalline phenylosazone which was free from water of crystallization and melted at 126° C after recrystallization from ether.

Oxidation with nitric acid by the procedure previously described produced the same dibasic dimethyl lactol acid which was obtained from the lower-boiling fraction of the hydrolyzed, partially methylated difructose anhydride III. Its calcium salt showed the following composition: Calculated for $C_8H_{10}O_8Ca.4H_2O$: H_2O, 20.8. Found:

20.77. Calculated for $C_8H_{10}O_8Ca$: OCH_3, 22.5; Ca, 14.57. Found: 22.6, 14.43.

6. 6-METHYLFRUCTOSE

3,4,3',4'-Tetra-acetyldifructose anhydride I.—Five grams of ditrityltetra-acetyldifructose anhydride I was dissolved in 20 ml of glacial acetic acid. To the solution, cooled to 5° C, was added 2 ml of acetic acid saturated with hydrogen bromide at 0° C, causing the precipitation of yellow trityl bromide. The filtrate was poured into an ice and water mixture, from which the tetra-acetyl derivative was extracted with chloroform. The chloroform solution was washed with sodium bicarbonate, dried over anhydrous sodium sulfate, and evaporated, leaving a sirupy residue. The latter was dissolved in absolute alcohol, from which the tetra-acetyldifructose anhydride crystallized in the form of rectangular plates. Yield, 1.8 g, or 53 percent of theory. Melting point, 173° C (uncor.). $[\alpha]_D^{20}=-9.9$ (chloroform, $c=3.73$); $+23.0$ (water, $c=2.96$). $OCCH_3$, calculated, 35.0. Found: 35.1.

A small portion upon acetylation yielded the hexa-acetyldifructose anhydride I described by Jackson and Goergen.

6,6'-Dimethyl 3,4,3',4'-tetra-acetyldifructose anhydride I.—Tetra-acetyldifructose anhydride I proved to be completely soluble in methyl iodide and was methylated with Purdie's reagents in the usual manner, three methylations being required to supply the full methoxyl content. At each stage of the methylation, however incomplete, the reaction product crystallized completely, giving a false indication of homogeneity. The fully methylated substance crystallized from aqueous alcohol in the form of prismatic needles. Melting point, 127° to 128° C (uncor.). $[\alpha]_D=+10.8$ (chloroform, $c=1.23$). OCH_3, calculated, 11.9. Found: 11.6.

6-Methylfructose and its osazone.—Dimethyltetraacetyldifructose anhydride I (0.51 g) was suspended in 17.5 ml of 0.8 *N* hydrochloric acid and heated at 95° C for a total of 45 minutes, which sufficed to hydrolyze the disaccharide and saponify the acetyl groups, as indicated by the constancy of rotation. The acid was removed as silver chloride and the filtrate treated with hydrogen sulfide. The filtrate was evaporated to dryness, dissolved in dry methyl alcohol containing 5 mg of hydrochloric acid per milliliter, and allowed to stand overnight. Hydrochloric acid was removed with silver carbonate and the filtrate treated at 10° C with dilute neutral potassium permanganate until a starch-iodide test showed a minute excess. The mixture was treated with a small amount of carbon and the filtrate evaporated, leaving a sirupy residue which distilled below 160° C at 0.01-mm pressure.

The distilled fructoside (0.2296 g), equivalent to 0.2116 g of 6-methylfructose, was hydrolyzed in 0.1 *N* hydrochloric acid at 60° C for 1 hour and was then diluted to 17.10 ml. The rotation in a 2-dm column was 0.46° (saccharimeter degrees); whence $[\alpha]_D^{26}=+6.4$ (0.06 *N* hydrochloric acid, $c=1.24$).

To the solution, after polarization, was added 0.2 g of hydrated sodium acetate, 4 ml of acetic acid, and 2 ml of redistilled phenylhydrazine. The mixture was heated for 40 minutes at 62° C, during which time abundant crystallization of the osazone occurred. The crystals, recrystallized from 95-percent alcohol, took the form of very long, fine, yellow needles. Melting point, 183° to 184° C (uncor.). $[\alpha]_D^{29}=-70.9$ (95-percent alcohol, $c=0.88$), diminishing to -55.6 in

18 days. *Analysis.* Calculated for $C_{19}H_{24}N_4O_4$: C, 61.27; H, 6.50; N, 15.04. Found: C, 61.22; H, 6.60; N, 15.00.

IX. SUMMARY

Difructose anhydrides I, II, and III, derived in about 5-percent yield from inulin which has been hydrolyzed by aqueous acids, are converted by methylation into hexamethyl derivatives which are purified by distillation. The derivatives of the first and third sugar are liquids, while that of the second is crystalline. Upon hydrolysis and distillation, I yields two molecules of 3,4,6-trimethylfructose, while III yields a mixture of two different trimethylfructoses, one of which is 3,4,6, as shown by its graded oxidation to trimethylarabonolactone.

Tritylation of III produces crystalline tritrityldifructose anhydride III which acquires, upon methylation, three methoxyl groups. Detritylation and hydrolysis cause the formation of a dimethyl and a monomethyl fructose, which are separated by fractional distillation of their fructosides. The dimethylfructose has a $[\alpha]_D^{20}=-60.66$ and forms an osazone of melting point 126° C. Its structure is shown by its oxidation to dibasic 3,4-dimethyl lactol acid, whose calcium salt is crystalline. The dimethyl fraction is therefore 3,4-dimethylfructose.

The monomethylfructose yields a monomethylglucosazone, which melts at 156° C and is identical with that prepared from 4-methylglucose. It is shown that when mixed with 3- or 6-methylglucosazone, the only other possible monomethyl compounds which could be formed, the melting point is depressed. The monomethyl derivative is thus 4-methylfructose.

Difructose anhydride III is therefore constituted of two fructose residues with oxygen bridges connecting, respectively, carbons 1 and 2 of the one residue with 2 and 3 of the other. Its great stability is due to the presence of a dioxane ring, which serves as the connecting link between the two fructose groups.

The new derivatives of difructose anhydrides I and III which have been prepared in pure form are given in table 3. A system of nomenclature is tentatively suggested.

TABLE 3.—*Derivatives of difructose anhydrides*

DIFRUCTOSE ANHYDRIDE I	Melting point	$[\alpha]_D$	Solvent	Concentration
	°C			
Difructofuranose 1,2′,2,1′-anhydride	164	+27.0	Water	4.08
3,4,6,3′,4′,6′-Hexa-acetyldifructofuranose 1,2′,2,1′-anhydride.	137	+0.54	Chloroform	2.49
3,4,6,3′,4′,6′-Hexamethyldifructofuranose 1,2′,2,1′-anhydride.		+23.7	do	4.86
6,6′-Ditrityldifructofuranose 1,2′,2,1′-anhydride	195	+20.3	do	2.18
6,6′-Ditrityl 3,4,3′,4′-tetra-acetyldifructofuranose 1,2′,-2,1′-anhydride.	194	+21.06	do	3.73
3,4,3′,4′-Tetra-acetyldifructofuranose 1,2′,2,1′-anhydride	173	−9.9	do	3.73
6,6′-Dimethyl 3,4,3′,4′-tetra-acetyldifructofuranose 1,2′,-2,1′-anhydride.	127–8	+10.8	do	1.23
DIFRUCTOSE ANHYDRIDE III				
Difructofuranose 1,2′, 2,3′-anhydride	162	+135.64	Water	7.85
3,4,6,1′,4′,6′-Hexamethyldifructofuranose 1,2′,2,3′-anhydride.		+157.9	Chloroform	3.95
6,1′,6′-Tritrityldifructofuranose 1,2′, 2,3′-anhydride	127	+64.2	do	0.76
6,1′,6′-Tritrityl 3,4,4′-trimethyldifructofuranose 1,2′,2,3′-anhydride.		+70.2	do	1.05

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X. REFERENCES

[1a] R. F. Jackson and S. M. Goergen, BS J. Research **3,** 27 (1929) RP79.
[1b] R. F. Jackson and E. J. McDonald, BS J. Research **6,** 709 (1931) RP299.
[2] W. N. Haworth and H. R. L. Streight, Helv. Chim. Acta **15,** 693 (1932).
[3] J. C. Irvine and J. W. Stevenson, J. Am. Chem. Soc. **51,** 2197 (1929).
[4] E. W. Bodycote, W. N. Haworth, and C. S. Woolvin, J. Chem. Soc. **1932,** 2390.
[5] H. H. Schlubach and H. Knoop, Liebigs Ann. Chem. **504,** 25 (1933).
[6] W. N. Haworth and A. Learner, J. Chem. Soc. **1928,** 619.
[7] H. Hibbert, R. S. Tipson, and F. Brauns, Canadian J. Research **4,** 221 (1931).
[8] T. N. Montgomery, J. Am. Chem. Soc. **56,** 419 (1934).
[9] B. Helferich, Liebigs Ann. Chem. **440,** 1 (1924); Ber. deut. chem. Ges. **58,** 1605 (1925); **59,** 600 (1926); **62,** 1549 (1929); **63,** 959, 989 (1930).
[10] E. Pacsu, Ber. deut. chem. Ges. **58,** 1455 (1925).
R. Schinle, Ber. deut. chem. Ges. **65,** 319 (1932).
J. Munroe and E. G. V. Percival, J. Chem. Soc. **1935,** 874.
[11] J. C. Irvine and A. Hynd, J. Chem. Soc. **95,** 1220 (1909).
K. Freudenberg and R. M. Hixon, Ber. deut. chem. Ges. **56,** 2126 (1923).
C. G. Anderson, W. Charlton, and W. N. Haworth, J. Chem. Soc. **1929,** 1329.
[12] H. Ohle and L. Vargha, Ber. deut. chem. Ges. **62,** 2434 (1929).
R. Kuhn and W. Ziese, Ber. deut. chem. Ges. **59,** 2314 (1926).
B. Helferich and J. Becker, Liebigs Ann. Chem. **440,** 13 (1924).
[13] H. Herrissey, P. Fleury, and M. Joly, J. pharm. chim. [8] **20,** 149 (1934); cf. E. L. Jackson and C. S. Hudson, J. Am. Chem. Soc. **58,** 378 (1936), and many subsequent articles.
[14] H. H. Schlubach and H. Knoop, Liebigs Ann. Chem. **504,** 19 (1933).
[15] H. H. Schlubach and H. Elsner, Ber. deut. chem. Ges. **61,** 2363 (1928).
[16] W. N. Haworth, J. Chem. Soc. **107,** 8 (1915).
[17] W. N. Haworth and H. R. L. Streight, Helv. Chim. Acta **15,** 614 (1932); **15,** 693 (1932).
[18] F. Valentin, Collection Czechoslov. Chem. Communications **3,** 499 (1931). Method is given in detail by E. L. Jackson, R. C. Hockett, and C. S. Hudson, J. Am. Chem. Soc. **56,** 948 (1934).
[19] H. Meyer, Lehrbuch der Organisch-Chemischen Methodik, Vierte Auflage **1,** 671 (Julius Springer, Berlin, 1922).

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STABILITY OF BASE-METAL THERMOCOUPLES IN AIR FROM 800° TO 2,200° F

By Andrew I. Dahl

ABSTRACT

A study has been made of the changes in the emf of Chromel-Alumel and iron-constantan thermocouples heated in an oxidizing atmosphere at various temperatures and for various periods of time. The thermocouples were held at definite temperatures, ranging from 800° to 2,200° F, in steps of 200° F. Calibrations were made of the thermocouples in their original condition, and again after heating them at each temperature for total times of 10, 50, 100, 200, 400, 600, 800, and 1,000 hours, or as long as the thermocouples remained serviceable. The thermal emf of each element against platinum was measured in order to determine the relative stability of the individual elements. A few tests were made to determine the effect of wire size on the stability. The effects of changing the depth of immersion of thermocouples after they had been used under controlled conditions were also studied.

Since all tests were made in an atmosphere of clean air, the results give no information on stability except under oxidizing conditions.

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I. INTRODUCTION

With the widespread use of base-metal thermocouples for temperature measurement and control in industrial processes, there are numerous instances where high accuracy is of vital importance. Some processes require that a given temperature be maintained within narrow limits for an extended period of time, if efficiency in operation and uniformity in production are to be maintained. In order to meet these requirements, a more complete knowledge of the thermoelectric stability of base-metal thermocouple materials is necessary.

Practically all base-metal thermocouple wire produced in this country is annealed or given a stabilizing heat treatment by the manufacturer. For most purposes this treatment renders the product sufficiently stable, so that further changes which may occur while the thermocouple is in service may be neglected. However, when high accuracy is required throughout the useful life of the thermocouple,

these changes must be taken into account. In many industrial processes, thermocouples, when placed in service, are left undisturbed until there is evidence of either mechanical failure or of serious error in the temperatures indicated. However, long before this occurs, the thermocouple may have changed to such an extent as to make it unreliable for accurate temperature measurement. The changes in the thermoelectric characteristics of thermocouple materials due to ordinary service conditions are usually gradual and cumulative. They depend upon such factors as the temperatures encountered, the length of time in service, and the atmosphere surrounding the thermocouple. The various types of thermocouple materials are affected in various ways and to various degrees.

When the reference-junction temperature is maintained constant, the emf developed by a homogeneous thermocouple depends only on the temperature of the measuring junction. The emf developed by an inhomogeneous thermocouple depends not only on the temperature of the measuring junction but also on the temperature distribution throughout the inhomogeneous portions of the wires. All base-metal thermocouples become inhomogeneous with use at high temperatures. However, if all the inhomogeneous portions of the thermocouple wires are in a region of uniform temperature, the inhomogeneous portions have no effect upon the indications of the thermocouple. Therefore, an increase in the depth of immersion of a used couple has the effect of bringing previously unheated portions of the wires into the region of temperature gradient, and thus the indications of the thermocouple will correspond to the original emf-temperature relation, provided the increase in immersion is sufficient to bring all of the previously heated part of the wires within the zone of uniform temperature. If the immersion is decreased, the more inhomogeneous portions of the wires will be brought into the region of temperature gradient, thus giving rise to a change in the indicated emf. Furthermore, a change in the temperature distribution along inhomogeneous portions of the wire nearly always occurs when a couple is removed from one installation and placed in another, even though the measured immersion and the temperature of the measuring junction are the same in both cases. Thus the indicated emf is changed.

Although it is recognized that there are differences in composition and thermoelectric properties between various lots of thermocouple materials of the same general type, it is believed that the changes in the thermoelectric properties of a few selected lots of material will give a general idea of the changes which would occur in other lots of the same general type, provided that all the lots have received the same initial heat treatment.

II. MATERIALS INVESTIGATED

The thermocouple materials studied were Chromel *P*, Alumel, iron, and constantan. Chromel *P* and Alumel wire of No. 18 gage and iron and constantan of No. 14 gage were used for the tests at 800° and 1,000° F. For the tests at 1,200° F and above, No. 8 gage wires were used. To determine the relation of wire size to the thermoelectric stability, additional tests were made on No. 18 and No. 22 gage Chromel and Alumel at 1,200° and 1,600° F, and on No. 18 gage iron and constantan at 1,200° and 1,400° F.

Samples of the various materials were secured from several sources. Each of the materials used in the investigation had the temperature-emf relation characteristic of the large percentage of the material of its particular type now being manufactured. All of the wires had been heat treated by the manufacturers in the manner considered standard for the particular type of wire.

III. TEST METHODS

Since Chromel *P* is generally used in combination with Alumel, and iron with constantan, the materials were paired in this manner. In addition to determining the temperature-emf relation for each pair, the thermal emf of the individual elements of each pair against the platinum standard [1] Pt 27 was determined. In this way the thermoelectric changes of each thermocouple material were determined independently. The difference of the thermal emfs of the individual elements of a thermocouple against a third material is equal to the emf of the thermocouple. As all three were measured in this work, any two served as a check upon the third.

The temperatures were measured with a standard platinum to platinum—10 percent rhodium thermocouple calibrated in accordance with the specifications for the International Temperature Scale.[2] The platinum working standard used was checked periodically against Pt 27.

The pair or pairs of wire under test were insulated by two-hole porcelain insulators. The platinum reference wire was protected by a glazed porcelain tube and was sealed through the end of the protection tube with a Pyrex glass, leaving about 1 cm of the end of the wire protruding beyond the seal. The platinum-rhodium thermocouple, insulated with a two-hole porcelain tube inside a glazed porcelain protection tube, was likewise sealed through the end of its protection tube with a Pyrex glass, leaving the welded junction protruding about 1 cm beyond the seal. The ends of the base-metal wires, the platinum reference wire, and the standard thermocouple were then welded together to form a single composite junction.

The furnace used in this work was of the resistance type wound with platinum-rhodium wire. The furnace tube of Alundum was 60 cm long and 3-cm inside diameter. The wires under test, together with the platinum reference wire and the platinum-rhodium thermocouple, were placed in the furnace with the composite junction at about the midpoint. The wires were then securely clamped with respect to the furnace. Although the ends of the furnace tube were closed with asbestos wool to promote temperature uniformity, no attempt was made to exclude air from the heated chamber, so that the atmosphere prevailing within the tube was oxidizing. The reference junctions were maintained at 32° F during all the measurements. The temperature of the furnace was maintained practically constant during any observation at a given point by means of a hand-operated voltage regulator in the power circuit.

To obtain data on the effect of long-time exposure to high temperatures upon the thermoelectric properties of the materials, the following procedure was adopted. The initial measurements were made on the sample as received from the manufacturer. Measurements of the

[1] The thermoelectric reference standard maintained at the National Bureau of Standards.
[2] G. K. Burgess, BS J. Research **1**, 635 (1928) RP22.

thermal emfs of the various combinations were made at intervals of 200° F up to and including in each case the temperature at which the effect of heating was to be determined. The furnace was then allowed to cool to room temperature, and the measurements were repeated. The differences between the two sets of measurements were ascribed to the initial heating and will be referred to as the "initial changes." Similar measurements were then made after the materials had been held at the test temperature for total elapsed times of 10, 50, 100, 200, 400, 600, 800, and 1,000 hours, or as long as the materials remained serviceable. The test temperatures included every temperature from 800° F to and including 2,000 °F, in steps of 200° F. Chromel *P* and Alumel were also tested at 2,200° F. A fresh sample was used for the test at each temperature. During heating periods, the temperature of the furnace was maintained constant within ±5° F by means of an automatic temperature controller.

The procedure followed in studying the effect of decreasing the depth of immersion was as follows:

The materials were heated in the electric furnace for a period of 20 hours at a constant temperature. Following this heat treatment, the thermal emf of the samples was determined, the position of the samples being maintained the same as that during the 20-hour heating period. The furnace was then allowed to cool to room temperature, and the immersion was decreased 3 inches and the thermal emf determined in this new position. The difference between the observations for a given sample is due only to the change in immersion, since no heating took place between the two sets of measurements. This type of test was carried out on No. 8 gage iron and constantan at temperatures from 600° to 1,800° F, in 200° F steps, and on No. 8 gage Chromel *P* and Alumel from 600° to 2,200° F.

IV. RESULTS

1. TEMPERATURE EXPOSURE TESTS

(a) CHROMEL P AND ALUMEL

Figures 1 and 2 show the results obtained on No. 18 gage Chromel *P* and Alumel heated at 800° and 1,000° F, respectively. The changes in the completed Chromel-Alumel thermocouples are also shown. The changes in the individual elements are in the same direction, so that each becomes thermoelectrically positive to the material in its original condition. The convention followed in regard to sign is as follows:

If in a simple thermoelectric circuit the current flows from metal *A* to metal *B* at the colder junction, *A* is thermoelectrically positive to *B*. On the basis of this convention, Chromel *P* is positive to Alumel. Therefore, a positive change in Chromel *P* will increase the emf of a Chromel-Alumel thermocouple, while a positive change in Alumel will decrease the emf of the thermocouple. The changes observed in the tests at 800° and 1,000° F are small, in all cases less than the equivalent of 1° F for a Chromel-Alumel thermocouple.

Figures 3 to 8, inclusive, show the results obtained with No. 8 gage Chromel *P* and Alumel at temperatures from 1,200° to 2,200° F, inclusive. The changes in the emf of Chromel *P* are in the positive direction throughout all tests, with the exception of the test at 2,200° F, where a negative change was observed at temperatures above 1,600°

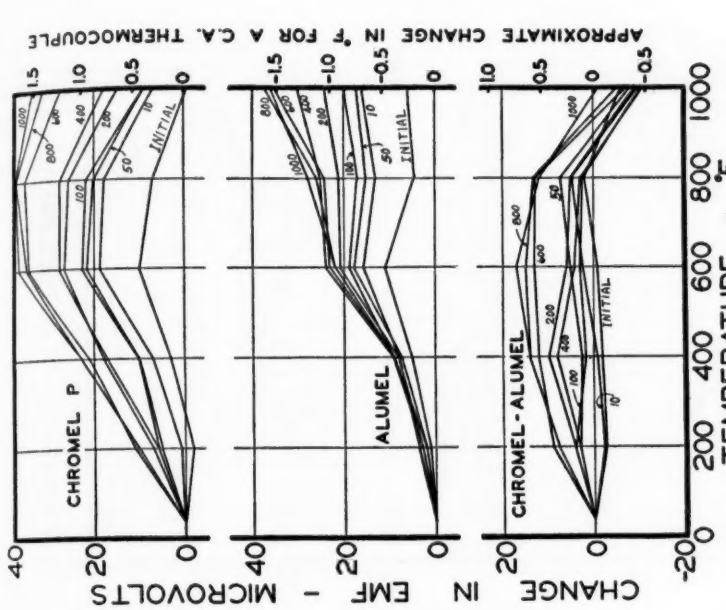

FIGURE 2.—*Changes in No. 18 gage Chromel P and Alumel due to heating at 1,000° F for the total times indicated on the graphs.*

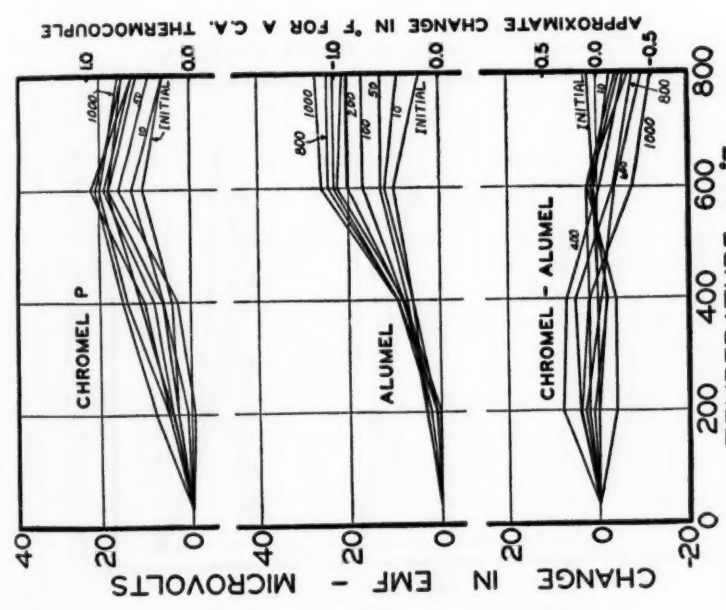

FIGURE 1.—*Changes in No. 18 gage Chromel P and Alumel due to heating at 800° F for the total times indicated on the graphs.*

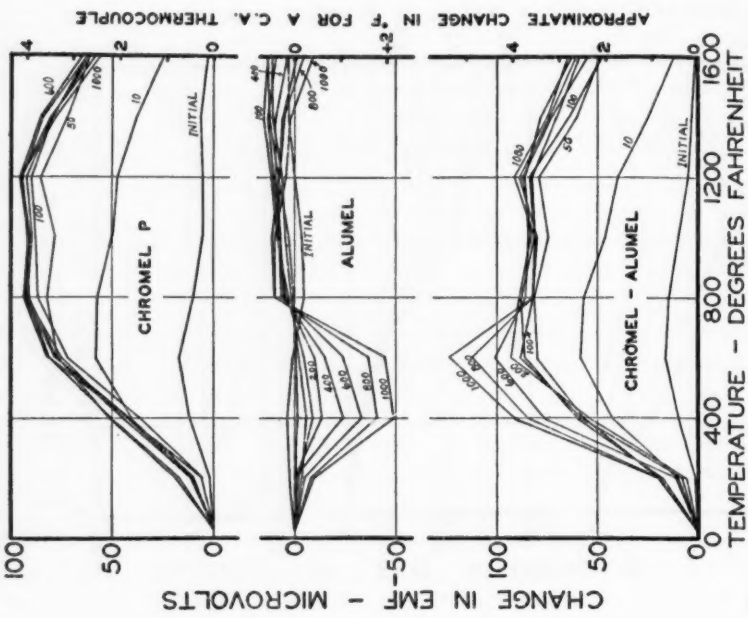

FIGURE 4.—*Changes in No. 8 gage Chromel P and Alumel due to heating at 1,400° F for the total times indicated on the graphs.*

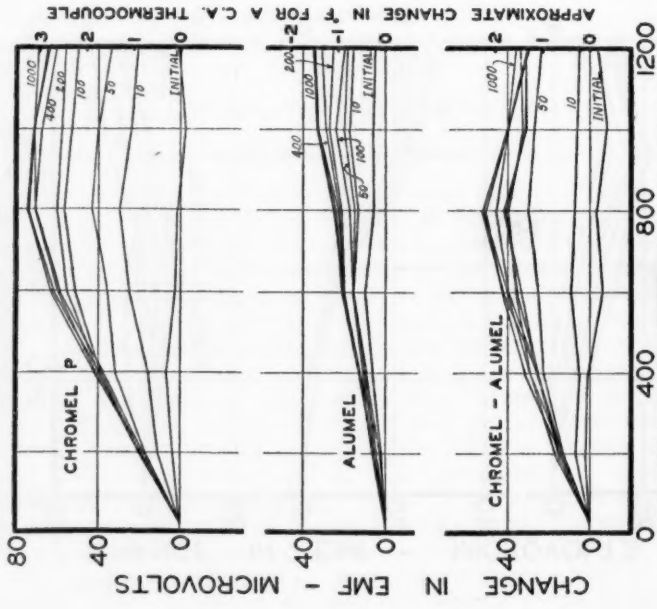

FIGURE 3.—*Changes in No. 8 gage Chromel P and Alumel due to heating at 1,200° F for the total times indicated on the graphs.*

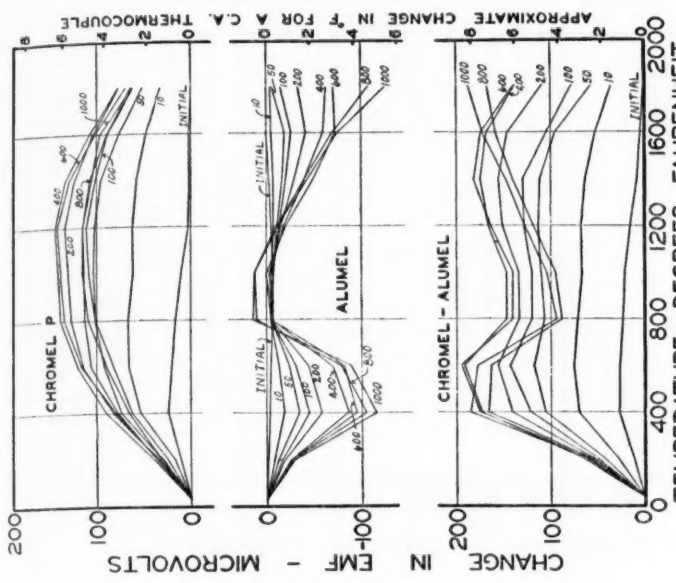

FIGURE 6.—*Changes in No. 8 gage Chromel P and Alumel due to heating at 1,800° F for the total times indicated on the graphs.*

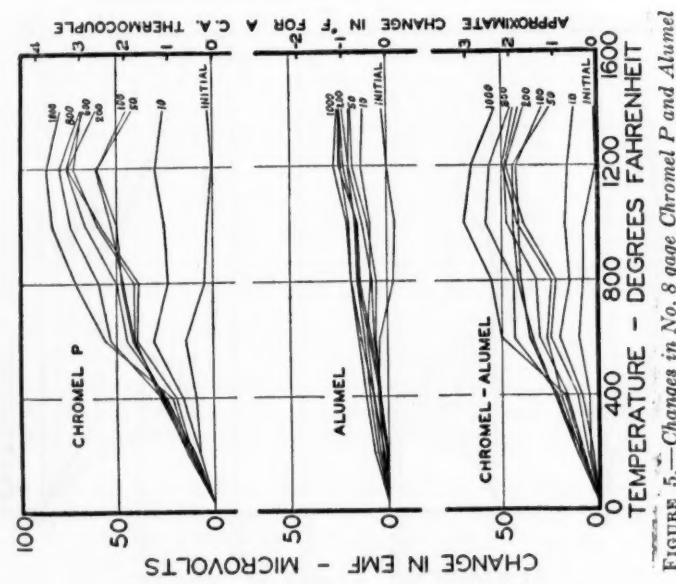

FIGURE 5.—*Changes in No. 8 gage Chromel P and Alumel due to heating at 1,600° F for the total times indicated on the graphs.*

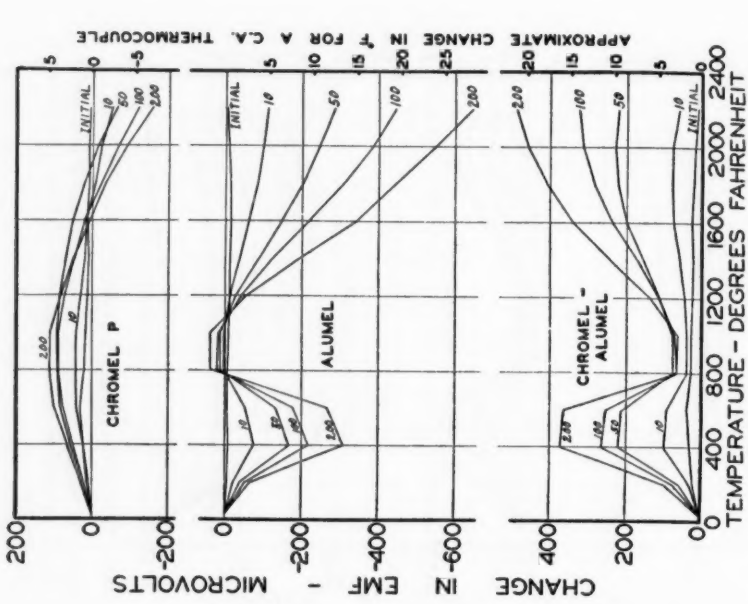

FIGURE 8.—*Changes in No. 8 gage Chromel P and Alumel due to heating at 2,200° F for the total times indicated on the graphs.*

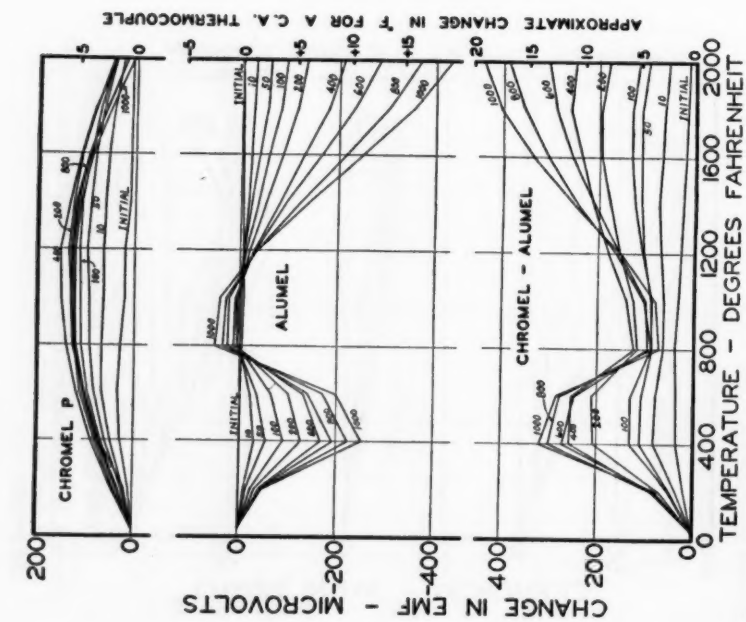

FIGURE 7.—*Changes in No. 8 gage Chromel P and Alumel due to heating at 2,000° F for the total times indicated on the graphs.*

F. The magnitude of the changes is, in nearly all cases, in the order of the duration of the heating periods, the maximum change occurring at about 1,200° F. The changes in the Alumel are in the positive direction throughout the tests at 1,200° and 1,400° F. In the tests at 1,600° F and above, the changes in the emf of the Alumel between about 800° and 1,100° F are extremely small. Above 1,100° F the changes are negative and of appreciable magnitude. This is most clearly shown in figure 7. The materials used in the test at 2,200° F failed after about 300 hours of heating.

Tests of No. 8, No. 18, and No. 22 gage Chromel-Alumel thermocouples heated at 1,200° F for a total of 1,000 hours indicated that

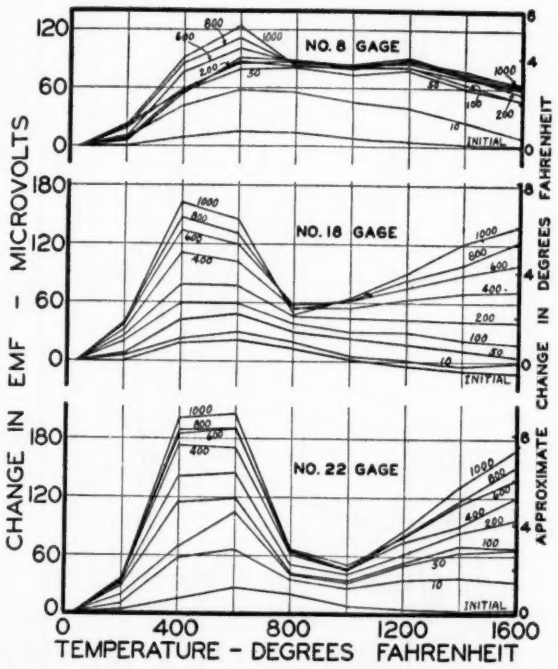

FIGURE 9.—*Changes in No. 8, No. 18, and No. 22 gage Chromel-Alumel thermocouples due to heating at 1,600° F for the total times indicated on the graphs.*

the changes in the thermocouples of the various sizes were nearly the same, and in all cases less than the equivalent of 2.5° F. Figure 9 shows the effects on the same sizes of Chromel-Alumel thermocouples when heated at 1,600° F. The change in calibration at 400° F is largest in the smallest size, but the reverse is true for the change at 1,000° F.

The changes in the emf of the Chromel-Alumel thermocouples produced by the total heating time in each of the tests are shown in figure 10 (reproduced from fig. 1 to 8, inclusive). In the test at 2,200° F the change after only 200 hours is shown, this being the elapsed time when the last measurements preceding failure were made. The peculiar change in the Alumel previously mentioned is reflected in change of the thermocouples.

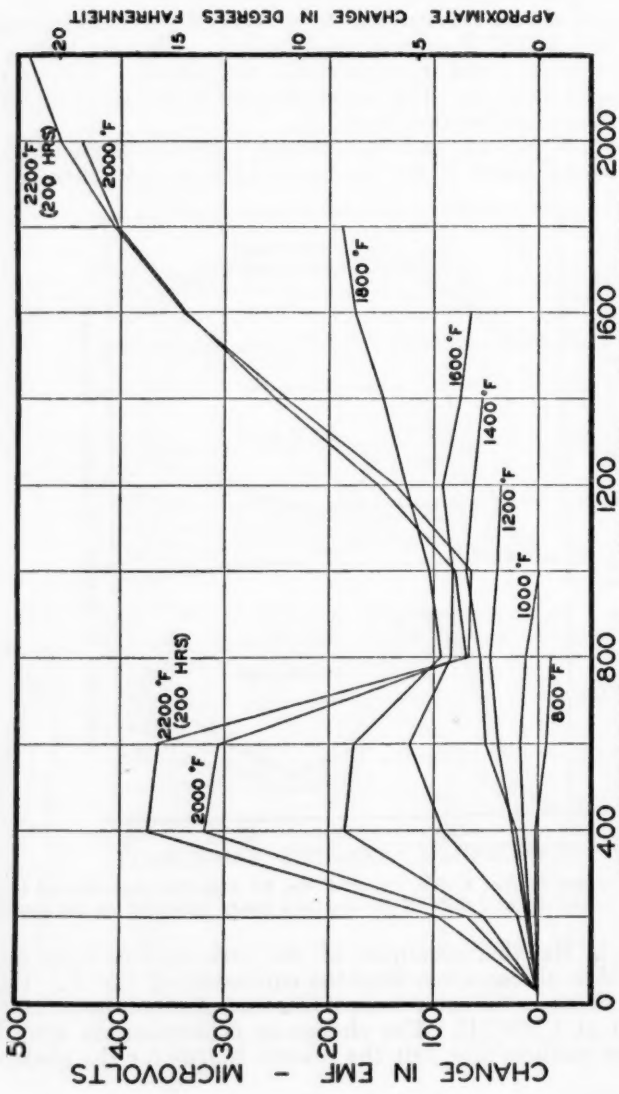

FIGURE 10.—*Changes in Chromel-Alumel thermocouples due to 1,000 hours of heating at temperatures indicated on the graphs.*

(b) IRON AND CONSTANTAN

Figures 11 and 12 show the results obtained on No. 14 gage iron and constantan tested at 800° and 1,000° F, respectively. The changes in all cases are small, being less than the equivalent of 1° F.

The results on No. 8 gage iron and constantan tested at 1,200° to 2,000° F, inclusive, are shown in figures 13 to 17. The time intervals between calibrations were shortened for the tests at 1,800° and 2,000° F, since at these temperatures the materials change at a rapid rate. The tests were continued until the materials failed.

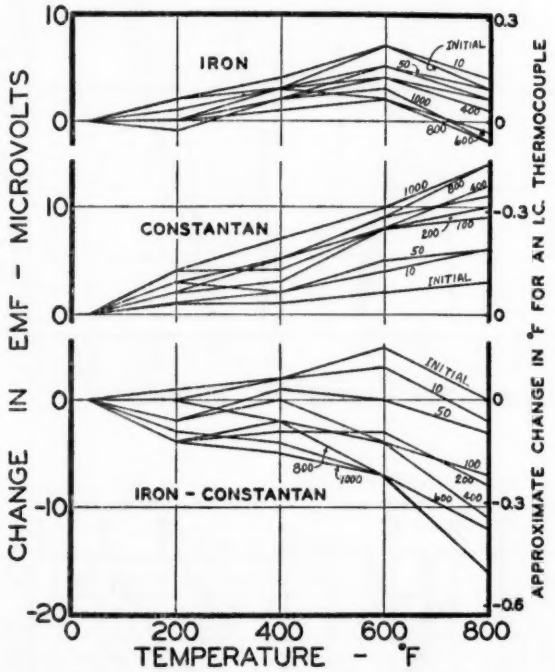

FIGURE 11.—*Changes in No. 14 gage iron and constantan due to heating at 800° F for the total times indicated on the graphs.*

The relative thermoelectric stability of No. 8 and No. 18 gage iron-constantan thermocouples heated at 1,400° F is shown in figure 18. As might be expected, the emf changes in the smaller wire proceed more rapidly. The No. 18 gage thermocouple failed after about 400 hours of heating, while the No. 8 gage remained serviceable throughout the 1,000 hours of the test. However, the measurements made on the thermocouple at the end of the 1,000-hour period indicated that failure was near. A test on these same sizes at 1,200° F showed no appreciable difference in their thermoelectric stability at this test temperature, the maximum change after 1,000 hours of heating being about the equivalent of 4° F.

The change in the emf of constantan was gradual and cumulative throughout each test. In the case of iron the change in emf was relatively small until failure of the wire was approached. When this stage was reached, the change was rapid and relatively large. This

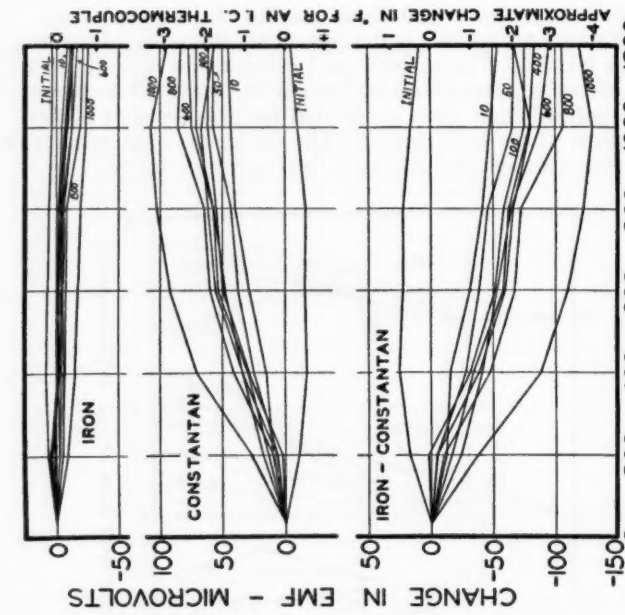

FIGURE 13.—*Changes in No. 8 gage iron and constantan due to heating at 1,200° F for the total times indicated on the graphs.*

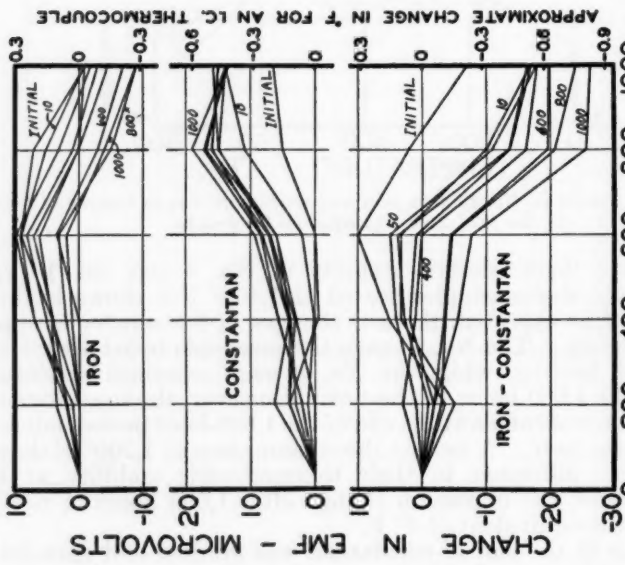

FIGURE 12.—*Changes in No. 14 gage iron and constantan due to heating at 1,000° F for the total times indicated on the graphs.*

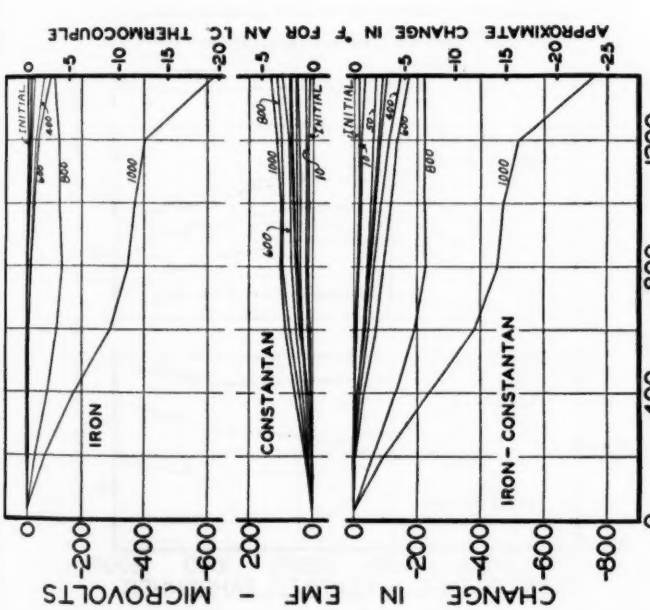

FIGURE 14.—*Changes in No. 8 gage iron and constantan due to heating at 1,400° F for the total times indicated on the graphs.*

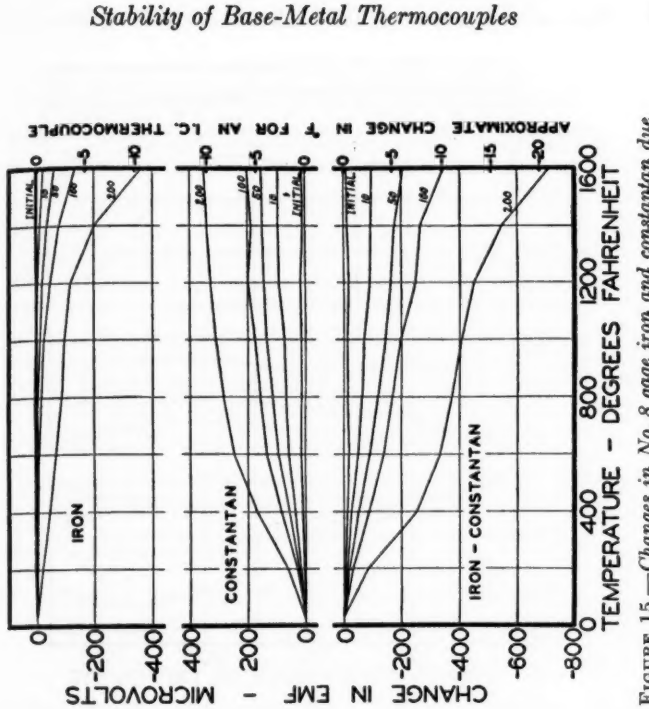

FIGURE 15.—*Changes in No. 8 gage iron and constantan due to heating at 1,600° F for the total times indicated on the graphs.*

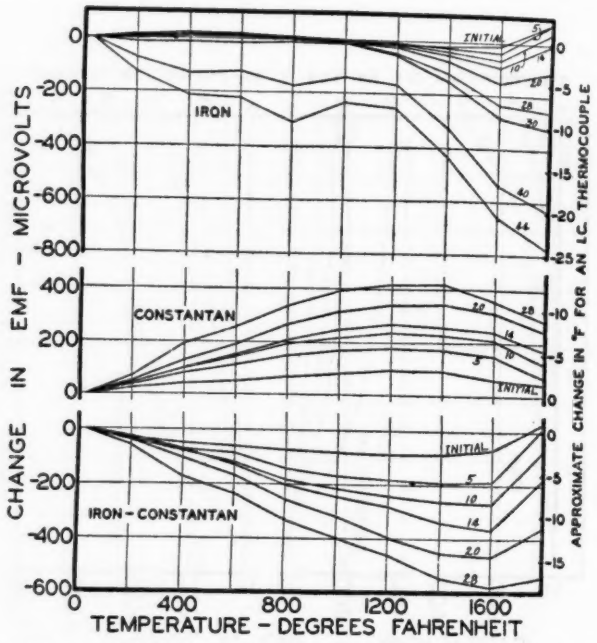

FIGURE 16.—*Changes in No. 8 gage iron and constantan due to heating at 1,800° F for the total times indicated on the graphs.*

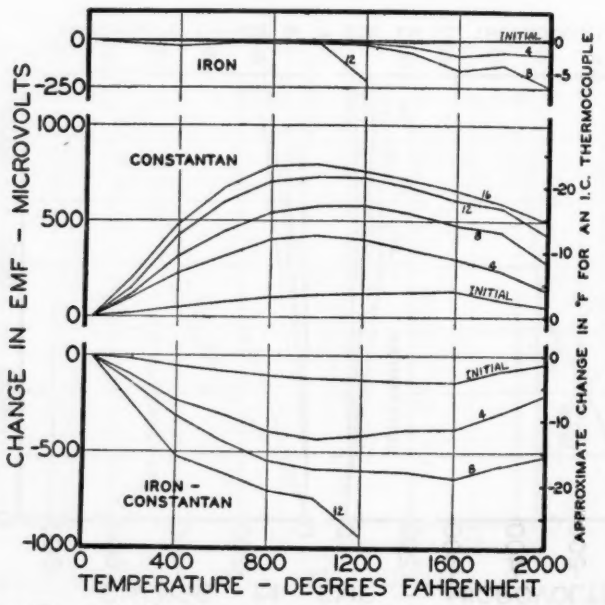

FIGURE 17.—*Changes in No. 8 gage iron and constantan due to heating at 2,000° F for the total times indicated on the graphs.*

was true for all tests in which iron was heated until failure occurred. The life of the iron element was found to be approximately the same as that of the constantan.

2. IMMERSION TESTS

Table 1 gives the observed changes in the thermal emf of No. 8 gage iron and constantan produced by a 3-inch decrease in immersion following the 20-hour heating period. The changes in both of the elements are gradual and regular throughout, the magnitude of the emf changes in constantan being everywhere considerably greater than in the case of iron. Figure 19 shows the change in the emf of the iron-constantan thermocouple under the various conditions of heating (test at 1,800° F not shown in graph). A greatly increased, though regular, change is clearly shown for the test at 1,600° F. At 1,800° F the change is about four times as great as that observed at 1,600° F.

TABLE 1.—*Changes (in thermal emf) at various temperatures caused by decreasing the depth of immersion 3 inches, after heating the wires in air at the temperatures indicated for 20 hours*

IRON

Calibration temperature	Heating temperature						
	600 °F	800 °F	1,000 °F	1,200 °F	1,400 °F	1,600 °F	1,800 °F
°F	μv	μv	μv	μv	μv	μv	μv
200	1	5	3	1	−2	−1	−2
400	0	7	4	3	−2	−4	−9
600	1	8	3	4	−2	−7	−18
800		7	2	4	−3	−12	−29
1,000			3	4	−6	−19	−43
1,200				1	−9	−30	−58
1,400					−13	−43	−72
1,600						−57	−80
1,800							−100

CONSTANTAN

200	4	10	13	14	14	25	83
400	7	18	20	30	28	62	224
600	9	27	26	43	41	93	374
800		35	37	52	53	127	504
1,000			49	60	54	156	615
1,200				65	65	182	735
1,400					68	208	837
1,600						223	935
1,800							1,078

IRON-CONSTANTAN

200	−3	−5	−10	−13	−16	−26	−85
400	−7	−11	−16	−27	−30	−66	−233
600	−8	−19	−23	−39	−43	−100	−392
800		−28	−35	−48	−56	−139	−533
1,000			−46	−56	−60	−175	−658
1,200				−64	−74	−212	−793
1,400					−81	−251	−909
1,600						−280	−1,015
1,800							−1,178

Table 2 gives the observed effects for No. 8 gage Chromel *P* and Alumel of changes in immersion, as outlined above. In the tests up to and including 1,600 °F the effect is gradual and approximately regular. At 1,800 °F and above, the Alumel element exhibited an irregular effect, somewhat similar to that observed in the exposure tests, which became more pronounced as the heating temperature was increased. Figure 20 illustrates the results for the Chromel-Alumel thermocouples.

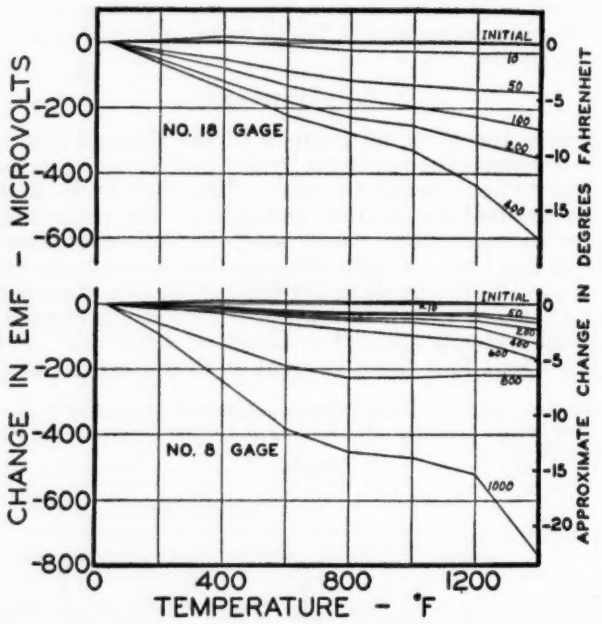

FIGURE 18.—*Changes in No. 8 and No. 18 gage iron-constantan thermocouples due to heating at 1,400° F for the total times indicated on the graphs.*

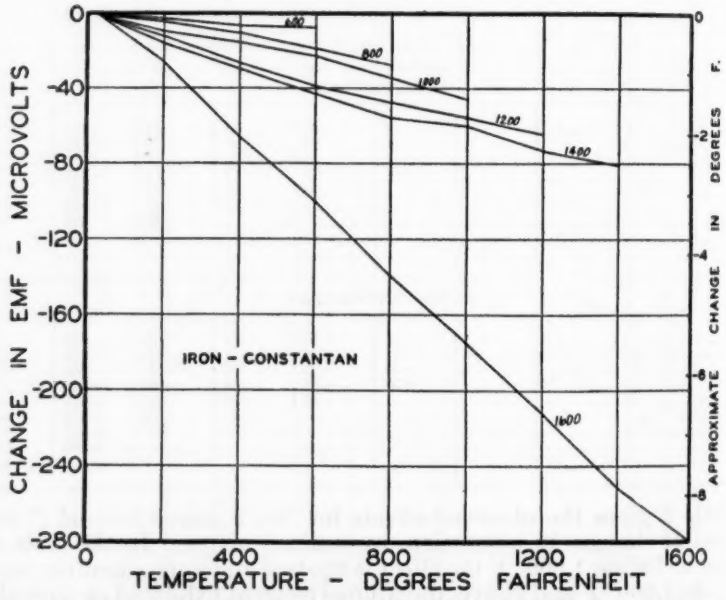

FIGURE 19.—*Changes in the indications of No. 8 gage iron-constantan thermocouples due to a 3-inch decrease in immersion after the couples had been heated for 20 hours at the temperatures indicated on the graphs.*

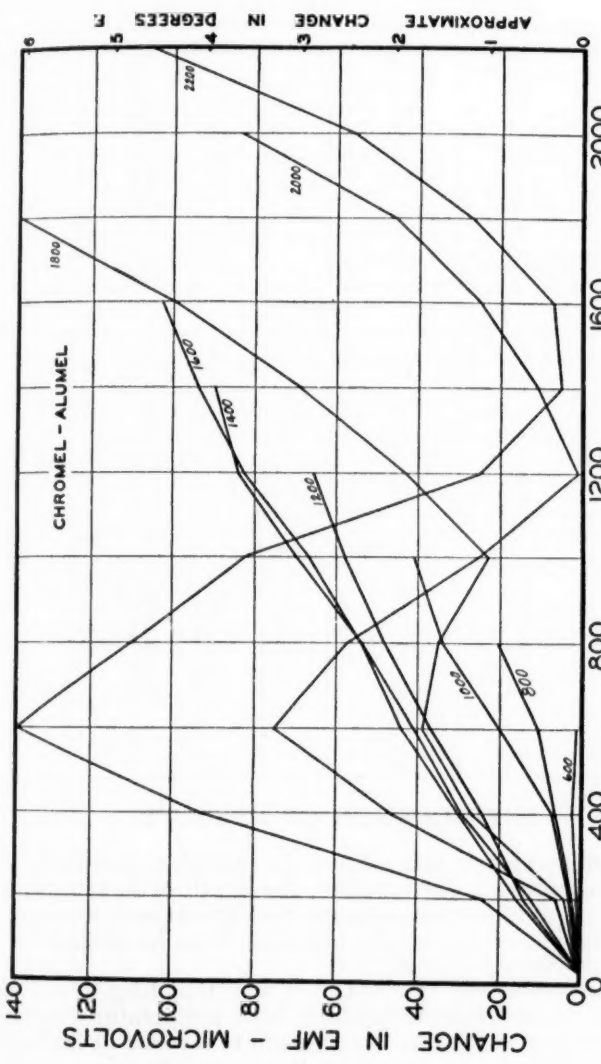

FIGURE 20.—*Changes in the indications of No. 8 gage Chromel-Alumel thermocouples due to a 3-inch decrease in immersion after the couples had been heated for 20 hours at the temperatures indicated on the graphs.*

TABLE 2.—*Changes (in thermal emf) at various temperatures caused by decreasing the depth of immersion 3 inches after heating the wires in air at the temperatures indicated for 20 hours*

CHROMEL *P*

Calibration temperature	Heating temperature								
	600° F	800° F	1,000° F	1,200° F	1,400° F	1,600° F	1,800° F	2,000° F	2,200° F
°F									
200	2	4	5	12	10	13	−1	−7	−7
400	5	9	8	21	25	24	+1	−12	−33
600	10	18	19	31	35	36	4	−14	−50
800		31	30	36	45	45	10	−16	−49
1,000			40	41	54	57	13	−21	−52
1,200				49	59	71	31	−32	−53
1,400					65	79	48	−28	−81
1,600						86	68	−29	−103
1,800							95	−28	−130
2,000								−18	−138
2,200									−176

ALUMEL

200	1	1	2	−2	−2	−3	−5	−13	−31
400	3	2	1	−3	−4	−6	−26	−59	−128
600	9	7	−1	−6	−6	−8	−35	−89	−193
800		10	−4	−12	−11	−9	−25	−73	−159
1,000			+1	−17	−17	−10	−10	−46	−131
1,200				−17	−25	−12	−13	−33	−78
1,400					−25	−15	−21	−39	−86
1,600						−17	−32	−54	−110
1,800							−45	−74	−137
2,000								−102	−214
2,200									−281

CHROMEL-ALUMEL

200	1	3	3	14	12	16	4	6	24
400	2	7	7	24	29	30	27	47	93
600	1	11	20	37	41	44	39	75	140
800		21	34	48	55	54	35	57	110
1,000			41	58	71	67	23	25	82
1,200				66	84	83	43	1	25
1,400					90	94	69	11	5
1,600						103	100	25	7
1,800							140	46	27
2,000								84	56
2,200									105

V. DISCUSSION OF RESULTS

As has been previously pointed out, the materials were heated in an oxidizing atmosphere. Furthermore, the depth of immersion of the materials in the furnace was constant throughout each exposure test. Direct application of the results obtained must be limited to cases where these conditions prevail.

From the observations reported, it is seen that long-time exposure of a Chromel-Alumel thermocouple to high temperatures causes the emf corresponding to a given temperature to increase or the temperature corresponding to a given emf to decrease. The effect on an iron-constantan thermocouple is just the reverse.

Failure of a Chromel-Alumel thermocouple (No. 8 gage) occurred within the 1,000-hour heating period only in the test at 2,200° F. In this case an open circuit was indicated after 300 hours, and examination of the sample showed that the metal forming the welded junction and the individual wires for some distance from the welded junction were oxidized nearly through.

The 1,000-hour heating periods at 2,000° and 1,800° F for No. 8 gage Chromel *P* and Alumel also produced appreciable oxidation of the materials. In the test at 2,000° F the diameter of the wires, after the oxide was removed, was 2.3 mm for the Alumel and 2.6 mm for the Chromel *P*, as compared with 3.3 mm for the original diameters. For the test at 1,800° F the diameter, after removing the oxide, was 2.6 mm for the Alumel and 3.1 mm for the Chromel *P*. In the tests at 1,600° F and below, the oxidation had not materially decreased the diameter of the wires.

The exposure tests on No. 8 gage iron-constantan thermocouples showed failure of the materials within the 1,000-hour heating time for the tests at 1,600° F and above. Failure occurred after 12 hours at 2,000° F, after 28 hours at 1,800° F, and after 300 hours at 1,600° F. The No. 18 gage iron-constantan thermocouple failed after about 500 hours at 1,400° F, while the No. 8 gage thermocouple remained serviceable throughout the 1,000-hour test at 1,400° F. However, at the conclusion of the test the diameters of the No. 8 gage materials had been reduced to about one-tenth of their original value.

A summary of the changes observed for Chromel-Alumel, iron-constantan, and Chromel-constantan thermocouples produced by long-time exposure to various temperatures is given in table 3. The values for Chromel-constantan were obtained indirectly by combining the changes in the individual elements. Though the changes in both Chromel *P* and constantan are considerably larger than those of the completed thermocouple, the directions are such that the changes counteract each other, so that the change in a Chromel-constantan thermocouple is small. The life of this thermocouple is limited by that of the constantan element.

TABLE 3.—*Changes in the calibration of base-metal thermocouples heated in air in an electric furnace*

Exposure temperature	Chromel-Alumel		Iron-constantan		Chromel-constantan	
	Hours of exposure	Maximum change	Hours of exposure	Maximum change	Hours of exposure	Maximum change
°F		°F		°F		°F
800	1,000	<1	1,000	<1	1,000	<1
1,000	1,000	<1	1,000	<1	1,000	<1
1,200	1,000	+2	1,000	−4	1,000	−1
1,400	1,000	3	800	−7	1,000	−2
1,600	1,000	5	100	−10	100	−4
1,800	1,000	8	28	−18		
2,000	1,000	19	8	−19		
2,200	200	21				

The relatively large changes in calibration observed for Chromel-Alumel thermocouples at 400° and 600° F, after the couples have been exposed to temperatures of 1,600° F and above, are not as serious as may at first appear. When a thermocouple is used for accurate measurement of temperatures of 1,600° F or above, it is seldom required that this same couple be used for accurate measurements at temperatures as low as 400° or 600° F. Therefore, the relatively large changes at these lower temperatures are of no great importance. A thermocouple which is to be used for accurate measurements below 1,000° F should not be exposed to the higher temperatures. If this

procedure is followed, the relatively large changes at 400° and 600° F will be avoided.

The results on the immersion tests emphasize the importance of never decreasing the depth of immersion of a thermocouple after it has once been placed in service. The practice of using a single base-metal thermocouple for high-temperature measurements in a number of different installations should be avoided. It is even difficult to obtain consistent and accurate results by using a thermocouple in a single installation if the couple is withdrawn and replaced between periods of service. The results obtained by removing a used base-metal couple from an installation to determine the corrections to the original calibration by testing it in a laboratory furnace are unreliable. The temperature gradients in the two furnaces usually differ widely, and hence the results will not be applicable to the actual service conditions. If it is practicable by any means to remove the inhomogeneous portions of the thermocouple from the temperature gradient, then the original calibration of the couple is applicable.

WASHINGTON, December 14, 1939.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

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PREDICTIONS OF NORMAL RADIO CRITICAL FREQUENCIES RELATED TO SOLAR ECLIPSES IN 1940

By Newbern Smith

ABSTRACT

The ordinary-wave critical frequencies of the E, F_1, F_2, and night F layers are predicted for use in ionospheric eclipse observations during the annular solar eclipse of April 7, 1940, and the total solar eclipse of October 1, 1940. The probable reliability and range of application of the data are discussed.

In connection with preparations for ionosphere observations during the solar eclipses of April 7 and October 1, 1940, it is of interest to know the average values of the normal critical frequencies which may be expected in the paths of the eclipse. It is the purpose of this note to give estimates of the expected average values of the ordinary-wave critical frequencies of the E, F_1, F_2, and night F layers.

The annular eclipse of April 7 will be observable in northern Mexico and the southern United States. Figure 1 gives the estimated monthly average critical frequencies for a place in Texas 29° N and 100° W for that month. Figure 2 gives the estimated values for Washington, D. C., for the same month. All predictions are given in terms of monthly averages, and the hours are local times at the given places. The Washington values were obtained by the same procedure as that used in preparing the monthly predictions published in the Proceedings of the Institute of Radio Engineers [1].[1] The Texas values were estimated by interpolating between the Washington data and the data for Huancayo, Peru, [2] 12° S and 75° W, for the same season. The graphs for Texas may be used for other locations in the United States in the path of the eclipse.

The total eclipse of October 1 will be observable in northern South America and in South Africa. Figure 3 gives estimated monthly average critical frequencies for Huancayo, Peru, 12° S and 75° W, for this month. These values may be considered as representative of the values to be encountered in northern South America. Figure 4 gives estimated monthly average critical frequencies for Watheroo, Western Australia, 30° S and 116° E, for October. It is believed that these values may be used for the South African location at approximately the same geographic latitude, although, owing to the differences in longitude and magnetic latitude, they may not be as reliable. The data of figures 3 and 4 were obtained by the same procedure as for Washington, using the available published data for Huancayo [2] and Watheroo [3].

[1] Figures in brackets indicate the literature references at the end of this paper.

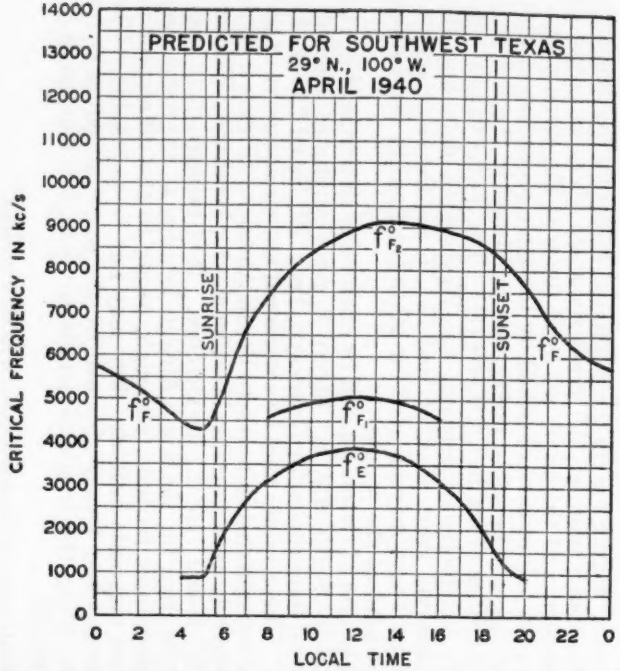

FIGURE 1.—*Predicted average critical frequencies of the E, F_1, F_2, and night F layers for undisturbed days in April 1940, for a place in Texas 100° W and 29° N.*

Abscissas are local times. These graphs may be used in northern Mexico or at other places in the southern United States whose latitudes are not much different from 29° N.

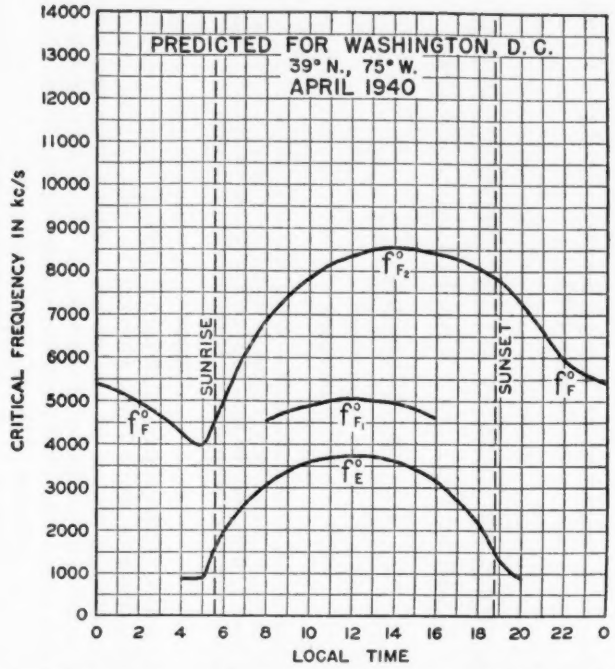

FIGURE 2.—*Predicted average critical frequencies of the E, F_1, F_2, and night F layers for undisturbed days in April 1940, for Washington, D. C.*

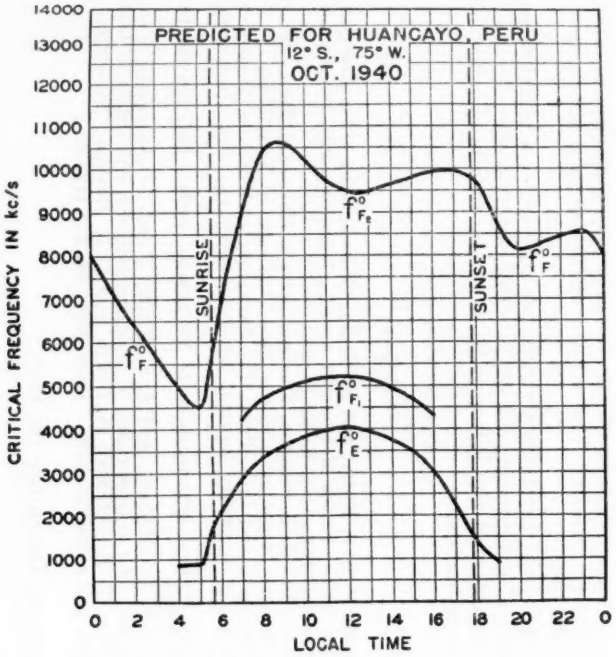

FIGURE 3.—*Predicted average critical frequencies of the E, F_1, F_2, and night F layers for undisturbed days in October 1940, for Huancayo, Peru, 75° W and 12° S.*

Abscissas are local times. These graphs may be used for places in northern South America whose latitudes do not differ greatly from 12° S.

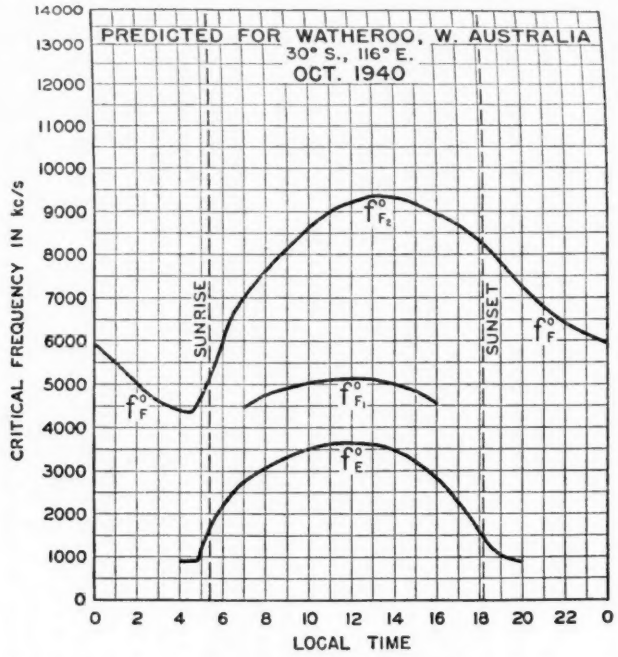

FIGURE 4.—*Predicted average critical frequencies of the E, F_1, F_2, and night F layers for undisturbed days in October 1940, for Watheroo, Western Australia, 116° E and 30° S.*

Abscissas are local times. These graphs may be used for places in South Africa whose latitudes do not differ greatly from 30° S.

The diurnal and seasonal variations and the year-to-year trends of the critical frequencies are based on published data for periods as follows:

Location	Day F_2 layer	E, F_1, and night F layers
Washington	1931 to Nov. 1939	May 1933 to Nov. 1939.
Huancayo	Jan. 1935 to Mar. 1939	Nov. 1937 to Mar. 1939.
Watheroo	Feb. 1935 to Mar. 1939	May 1938 to Mar. 1939.

The future year-to-year trends were estimated on the basis of an extrapolation of the present sunspot cycle by C. N. Anderson [4]. The correlation between the sunspot cycle and the trends of critical frequencies has been dealt with elsewhere [5].

The Washington predicted average is probably good within ±15 percent for undisturbed days, and the day-to-day variations from the monthly average are as given monthly in the Proceedings of the Institute of Radio Engineers [1]. The Texas values are probably but little less reliable. It is believed that the reliability of the Huancayo and Watheroo predictions is about as good, although data were not available over as long periods, and data on day-to-day variations were not available.

In conclusion, it is pointed out that the predictions are given for ionospherically undisturbed days only. If a disturbed day is encountered, the values observed may differ widely from the estimates, the difference being greater the nearer the observer is to one of the magnetic poles. An ionosphere storm, for example, partially, or in some cases completely, masked the eclipse effects during the eclipse of June 19, 1936 [6].

Nevertheless, the forecasts given above may serve a useful purpose in the design of equipment, the planning of observations, the evaluation of the data, and the interpretation of the results of ionospheric eclipse measurements.

References

[1] T. R. Gilliland, S. S. Kirby, and N. Smith, *Characteristics of the ionosphere at Washington, D. C.* Series of monthly reports, beginning with the September 1937 issue of the Proc. Inst. Radio Engrs.

[2] H. W. Wells and H. E. Stanton, *The ionosphere at Huancayo, Peru.* Series of quarterly reports, beginning with the June 1938 issue of Terr. Mag.

[3] W. C. Parkinson and L. S. Prior, *The ionosphere at Watheroo, Western Australia.* Series of quarterly reports, beginning with the June 1939 issue of Terr. Mag.

[4] C. N. Anderson, *A representation of the sunspot cycle.* Bell System Tech. J. **18,** 292 (1939).

[5] N. Smith, T. R. Gilliland, and S. S. Kirby, *Trends of characteristics of the ionosphere for half a sunspot cycle.* J. Research NBS **21,** 835 (1938) RP1159.

[6] S. S. Kirby, T. R. Gilliland, N. Smith, and S. E. Reymer, *The ionosphere, solar eclipse, and magnetic storm.* Phys. Rev. **50,** 258 (1936).

WASHINGTON, December 19, 1939.

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